This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`

DEPARTMENT OF COMMERCE

BULLETIN

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

LIBRARY
OF THE
UNIVERSITY
OF
CALIFORNIA

VOLUME 13

1916–17

UNIV. OF
CALIFORNIA

WASHINGTON
GOVERNMENT PRINTING OFFICE
1917

CONTENTS OF VOLUME 13

No. 1

[Issued June 15, 1916]

Page.
266. Preparation of Pure Iron and Iron-Carbon Alloys .... *J. R. Cain, E. Schramm,* and *H. E. Cleaves* 1
267. Colorimetric Determination of Acetylene and its Application to the Determination of Water .... *E. R. Weaver* 27
268. Constants of the Quartz-Wedge Saccharimeter and the Specific Rotation of Sucrose. I. The Constants for the 26-Gram Normal Weight .... *Frederick Bates* and *Richard F. Jackson* 67
269. Effect of Imperfect Dielectrics in the Field of Radio-Telegraphic Antenna .... *John M. Miller* 129
270. Luminosity of a Black Body and Temperature .... *Paul D. Foote* and *C. O. Fairchild* 137
271. Inclusions in the Silver Voltameter Deposits .... *G. W. Vinal* and *William M. Bovard* 147

No. 2

[Issued August 19, 1916]

272. Correlation of the Magnetic and Mechanical Properties of Steel .... *Charles W. Burrows* 173
273. General Design of Critically Damped Galvanometers. *Frank Wenner* 211
274. Interference Measurements of Wave Lengths in the Iron Spectrum (3233A–6750A). *Keivin Burns, W. F. Meggers,* and *Paul W. Merrill* 245
275. Relation Between Composition and Density of Aqueous Solutions of Copper Sulphate and Sulphuric Acid .... *H. D. Holler* and *E. L. Peffer* 273
276. Protected thermoelements .... *Arthur W. Gray* 283
277. An Interlaboratory Photometric Comparison of Glass Screens and of tungsten Lamps, Involving Color Differences .... *G. W. Middlekauff* and *J. F. Skogland* 287
278. An Investigation of the Laws of Plastic Flow. *Eugene C. Bingham* 309

No. 3

[Issued December 30, 1916]

279. Distribution of Energy in the Visible Spectrum of an Acetylene Flame .... *W. W. Coblentz* and *W. B. Emerson* 355
280. Further Experiments of the Volatilization of Platinum .... *G. K. Burgess* and *R. G. Waltenberg* 365
281. A Study of the Inductance of Four-Terminal Resistance Standards .... *Francis B. Silsbee* 375
282. Sensitivity and Magnetic Shielding Tests of a Thomson Galvanometer for Use in Radiometry .... *W. W. Coblentz* 423

351549

GIFT OF

SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS

LVX
FIAT

MDCCCLXVIII

EX LIBRIS

No. 1

RDS

Page

ves 1
na-
ver 27
of

son 67

ller 120
hill 137
rd 147

V. 13 comple

DEPARTMENT OF COMMERCE

Vol. 13 No. 1

BULLETIN

OF THE

BUREAU OF STANDARDS

S. W. STRATTON, DIRECTOR

ISSUED JUNE 15, 1916

CONTENTS

Page
Preparation of Pure Iron and Iron-Carbon Alloys . . . . *J. R. Cain, E. Schramm, and H. E. Cleaves* 1
Colorimetric Determination of Acetylene and Its Application to the Determination of Water . . . . *E. R. Weaver* 27
Constants of the Quartz-Wedge Saccharimeter and the Specific Rotation of Sucrose. I. The Constants for the 26-Gram Normal Weight . . . . *Frederick Bates and Richard F. Jackson* 67
Effect of Imperfect Dielectrics in the Field of a Radiotelegraphic Antenna . . . . *John M. Miller* 129
Luminosity of a Black Body and Temperature . *Paul D. Foote and C. O. Fairchild* 137
Inclusions in the Silver Voltameter Deposits . *G. W. Vinal and William M. Bovard* 147

WASHINGTON
GOVERNMENT PRINTING OFFICE
1916

I. INTRODUCTION

The fundamental importance of the iron-carbon thermal equilibrium diagram in the scientific metallurgy of iron and steel and its utility to practical workers have long been realized, and accordingly this subject has received attention from many points of view and from many investigators during the past two decades.

In view of this fact, it might seem superfluous to add to the existing literature except for the following considerations: Earlier workers have for the most part confined their attention to special portions of the diagram or to disputed questions of theory. Their thermal studies have not been carried out with the degree of accuracy now attainable. They have practically without exception employed commercial materials of varying degrees of purity. In two papers published in 1913[1] Prof. H. M. Howe, as a result of a thorough examination of the literature, has fixed the most probable position of the equilibrium lines. His net conclusions are that "this calculated line is not entitled to great weight because of the weakness of the evidence," and that "much better data are needed, reached with pure materials and with the many causes of error reduced to a minimum." In Table 1, compiled from Prof. Howe's papers, are given analyses of the materials used in some of the more important recent investigations. A glance at the table will show the justice of the conclusions quoted above. The analyses are incomplete even for the impurities ordinarily determined, and entirely ignore the possible presence of other impurities, such as Cu and Ni; but so far as they go, they indicate a very appreciable degree of contamination by S, Si, Mn, elements which we know exert a marked effect on the critical ranges. It may be said that the iron-carbon diagram has never been worked out with pure iron-carbon alloys. The present paper describes the preparation of a series of high degree of purity, to be used as the basis of a more accurate study of the equilibrium diagram than has heretofore been attempted.

---

[1] Ae_1, the Equilibrium Temperature for A_1 in Carbon Steel, Bull. Am. Inst. Min. E., p. 1066; 1913. A Discussion of the Existing Data as to the Position of Ae_3, Bull. Am. Inst. Min. E., p. 1099.

TABLE 1

Composition of Iron-Carbon Alloys Used by Various Investigators in Determinations of Critical Points

No.	Authority	Date	Composition of specimens				
			C	Si	Mn	P	S
			Per cent	Per cent	Per cent	Per cent	Per cent
1	Carpenter and Keeling [a]	1904	0.38	0.06	Trace.	0.03	0.01
2	.....do	....	1.85	.09	....	....	....
3	.....do	....	3.98	....	....	....	....
4	.....do	....	4.50	.12	....	....	....
5	.....do	....	2.63	....	....	....	....
5A	.....do	....	2.85	....	....	....	....
6	.....do	....	2.85	....	Trace?	....	....
7	Heyn [b]	1904	.39	.04	.03	....	....
8	.....do	....	.95	.04	.06	....	....
9	Rosenhain [c] (on Brayshaw's steel A2)	1910	1.14	.09	.40	.014	.018
10	.....do	....	....	....	....	....	....
11	Benedicks [d]	1908	1.00	....	.25	....	....
12	Charpy and Grenet [e]	1903	.64	....	....	....	....
13	.....do	....	.64	....	....	....	....
14	.....do	....	.93	....	....	....	....
15	.....do	....	.93	....	....	....	....
16	.....do	....	1.50	....	....	....	....
17	Brayshaw [f] No. W4	1910	1.15	.21	.31	.011±	.012±
18	Brayshaw No. W2	1910	1.16	.10	.37	.014	.023
19	Brayshaw No. A2	....	1.14	.09	.40	.014	.018
20	Levy [g]	1913	.23	.039	.05	.013	.010
21	Levy	1912	.92	.14	.123	.009	.011
22	Howe and Levy [h]	1913	.027	....	.26	.005	.024
23	.....do	....	.105	.013	.24	.015	.028
24	.....do	....	.214	.039	.05	.013	.010
25	.....do	....	.227	.039	.05	.013	.010
26	.....do	....	.235	.039	.05	.013	.010
27	.....do	....	.244	.050	Nil.	Nil.	.007
28	.....do	....	.382	.027	.22	....	.004
29	.....do	....	.40	.103	.16	.014	.012
30	.....do	....	.563	.18	.15	.013	.013
31	.....do	....	.59	.144	.17	.018	.013
32	.....do	....	.73	.141	.07	.012	.019
33	.....do	....	.92	.14	.123	.009	.011

---

[a] Carpenter and Keeling, Journal Iron and Steel Inst., 65, p. 244; 1904, No. 1; Collected Researches of the Nat'l Phys. Lab., 1, p. 227.

[b] Heyn, Verh. des Vereins zur Beförderung des Gewerbfleisses, p. 371; 1904.

[c] Rosenhain, Proc. Inst. Mech. Engrs., p. 688; 1910, parts 1 and 2.

[d] Benedicks, Jour. Iron and Steel Inst., 77, p. 218; 1908, No. 2.

[e] Charpy and Grenet, Bulletin Soc. d'Encouragement pour l'Industrie Nationale, p. 480; 1903, No. 1.

[f] Brayshaw, Proc. Inst. Mech. Engrs., pp. 525, 537, 656, 670; 1910, parts 1 and 2.

[g] Howe, Bull. Amer. Inst. Min. Engrs., p. 1068; 1913, No. 1.

[h] Howe and Levy, Bull. Amer. Inst. Min. Engrs., p. 1076; 1913, No. 1.

For the production of pure iron on a fairly large scale, the electrolytic refining method was obviously most suitable and was therefore adopted in this work. Pure carbon was made by calcining in a Dixon graphite crucible the pure sugar used as stock for Bureau of Standards analyzed sample No. 17. The latter contains, as the only impurity of importance for present purposes, 0.003 per cent ash, and the carbon obtained from it has an ash content of 0.17 per cent.

II. MAKING THE ELECTROLYTIC IRON

The electrolytic method, using soluble anodes, has been frequently employed in similar investigations[2] and its essentials are well known, so that we give details only for the sake of completeness and because, in one respect, our method deviates from that usually followed, namely, in the use of porous anode compartments. The first iron was made on a small scale. The essential details of the bath are as follows: Two cylindrical anodes of ingot iron[3] about 2 inches in diameter by 5 inches long, contained in porous clay cups; three cathodes of sheet iron, each 4 inches square; electrolyte, 25 to 30 per cent $FeCl_2$ solution (made by dissolving the ingot iron in chemically pure hydrochloric acid), prepared as nearly neutral as possible; current density about 0.5 to 0.7 ampere per square decimeter; temperature during electrolysis approximately that of the room. No attempt was made to determine the yield or to secure high current efficiency. Good adherent deposits were obtained, the greatest thickness being about 0.5 cm. Owing to the unfavorable current distribution when working with anodes and cathodes of such unequal sizes, the thickness of deposit was not uniform all over the plates. Qualitative tests of the sludge from the anode cells showed that there was an accumulation of manganese and copper derived from anodic impurities. The porous cups therefore seemed to be of service in preventing anode impurities from migrating to the cathodes, and they were accordingly used in one of the larger baths to be described later. In another similar tank the cups were omitted. Table 2 shows that the cathode deposits from the bath without the cups were a little higher in copper than the others but were otherwise of similar quality. It was found that there was much oxidation of the surface layers of electrolyte as the electrolysis went on, resulting in the production of basic salts of iron, which floated in the bath and which migrated to some extent to the cathodes. With the intention of avoiding or minimizing this oxidation, the small bath was provided with a hydraulically sealed cover having windows for observation and conduits for the current leads. The air in the space over the electrolyte was displaced with purified carbon dioxide and the electrolysis conducted as before. This method led to no marked improvement and it was abandoned, especially as there seemed to be a tendency toward higher percentages of carbon in the cathodic deposits. Although the greater part of the sediment settled to the bottom, the bath was never quite free from turbidity caused by these basic salts, and there is no doubt that the deposits were contaminated by them in slight degree. This was of no consequence, inasmuch as these impurities were either volatilized or were reduced to iron in subsequent melting operations. The analysis of the iron stripped from cathodes of the small electrolytic bath is given in Table 2. About 2 or 3 kg was made in this bath.

---

[2] See bibliography at end of this paper.

[3] Analysis as follows: C, 0.016; S, 0.022; Mn, 0.029; P, 0.001; Si, 0.002; and Cu, 0.15.

TABLE 2

Analyses of Electrolytic Iron from Various Sources

Source	C	S	P	Mn	Si	Cu	Ni and Co	Total impurity	Analysis by—
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	
1[a, b]	0.004	0.002	Trace	Trace	0.003	0.006	0.011	0.026	B. S.
2[c, b]	.004	.003	Trace	Trace	.006	Trace	.011	.024	B. S.
3[d, b]	.004	.006	Trace	Trace	.008	.006	.011	.035	B. S.
4[e]	.004	.004	Trace	Trace	.005	.008	.011	.033	B. S.
5[f]	.063	.002	0.005	0.009	.005	....	....	.084	Müller
6[g]	.008	Trace	.002	.009	.014	....	....	.033	Stead
7[h]	.008	.004	Trace	Trace	.006	.011	....	.029	B. S.
8[i]	.009	.003	Trace	Trace	.006	.006	....	.024	B. S.

[a] B. S. (with porous cups).

[b] Bureau of Standards analysis of anodes from which this iron was made: C, 0.013 per cent; S, 0.020 per cent; P, 0.003 per cent; Mn, 0.025 per cent; Si, 0.003 per cent; Cu, 0.024 per cent; and Ni+Co, 0.021 per cent. (Cf. Burgess and Crowe, this Bulletin, 10, p. 342; 1914.

[c] B. S. (with porous cups).

[d] B. S. (without porous cups).

[e] B. S. (from small tank).

[f] A. Müller, Metallurgie, 6, p. 152; 1909.

[g] H. C. H. Carpenter.

[h] Langbein-Pfanhauser.

[i] C. F. Burgess.

The large electrolytic bath is shown in Fig. 1. The anode cups were molded from a mixture of equal parts by volume of alundum cement and of clean white Ottawa sand; after careful drying in an oven the cups were burned at a temperature of 1000° to 1100° and were then found to have a satisfactory degree of porosity. The current density during electrolysis varied from 0.3 to 0.4 amperes per square decimeter. The electrolyte contained 23.3 per cent $FeCl_2$ (made from the ingot iron previously described) and 10.3 per cent NaCl, and was nearly neutral. Analyses of electrolyte from the anode and cathode compartments made after a week's run were as follows:

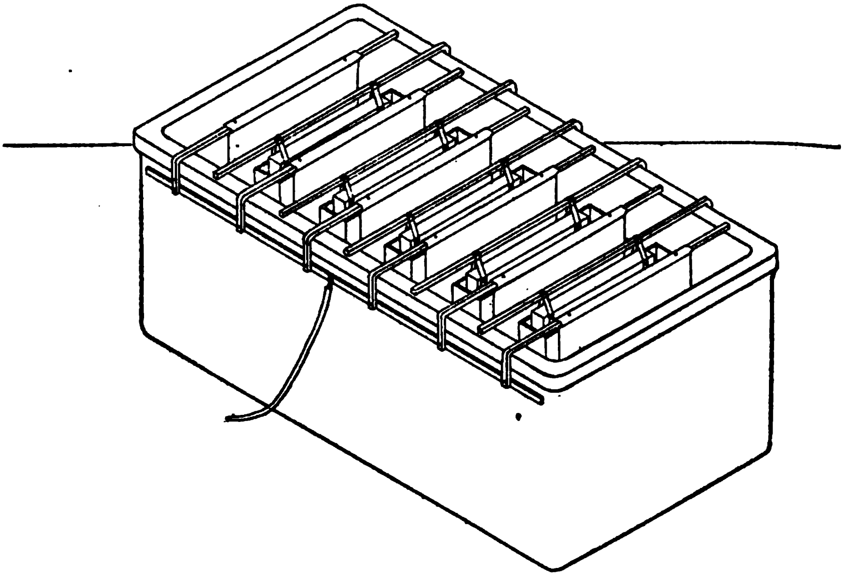


FIG. 1.—*Tank for preparing electrolytic iron*

	Anode compartment	Cathode compartment
Per cent iron, original	9. 52	7. 88
Per cent iron after one week's run	8. 82	7. 53

The character of the deposits is shown by Figs. 2, 3, and 4. Deposits of 5 to 7 mm thickness were obtained; the characteristics of these were about the same as of those made in the smaller bath. They were very hard and brittle in consequence of contamination by hydrogen. On removal from the bath and after washing with distilled water they corroded rapidly in the air. No account was taken of this surface oxidation, inasmuch as the iron was to be used for making iron-carbon alloys in such a way that the oxidized compounds of iron would be reduced to metal and the hydrogen expelled. About 12 to 15 kg of iron was made for use in preparing the alloys. In Table 2 are given analyses of this iron made with and without the use of porous anode compartments, and for comparison analyses of electrolytic iron from other sources.

III. MELTING THE ELECTROLYTIC IRON

The next step for the further utilization of the electro-deposited iron is to melt it into ingots. As already stated, the material as taken from the bath is brittle and is contaminated with occluded chlorides from the electrolyte, with hydrogen, and with oxidized compounds of iron. Annealing at 600° to 800° suffices to remove most of the hydrogen and some of the chlorides; this renders the iron more malleable and resistant to corrosion, but to attain a still higher degree of purity and to simplify subsequent operations the iron must be fused, preferably in a reducing atmosphere, and held in a state of fusion for some minutes. Owing to the high melting point of iron (1530°), to its strong tendency to combine with or to be contaminated by substances likely to be present as vapors in electrically heated furnaces (Si, S, C, Pt, and the like), or as gases in the products of combustion of a fuel-fired furnace (CO, SO_2, SO_3, CO_2, H_2O), and especially because of the corrosive action on crucibles of molten oxides of iron, with resulting possible contamination of the melt by slags, etc., it is evident that great care must be taken in the choice of furnaces and crucibles for work of this kind. While it is true that iron in the molten condition containing as little as 0.1 to 0.2 per cent of the impurities ordinarily determined has been produced commercially for some time, the conditions of laboratory preparation on a small scale are entirely different and lead to new difficulties: (1) Contamination by the hearth, or crucible material, or by gases is less in

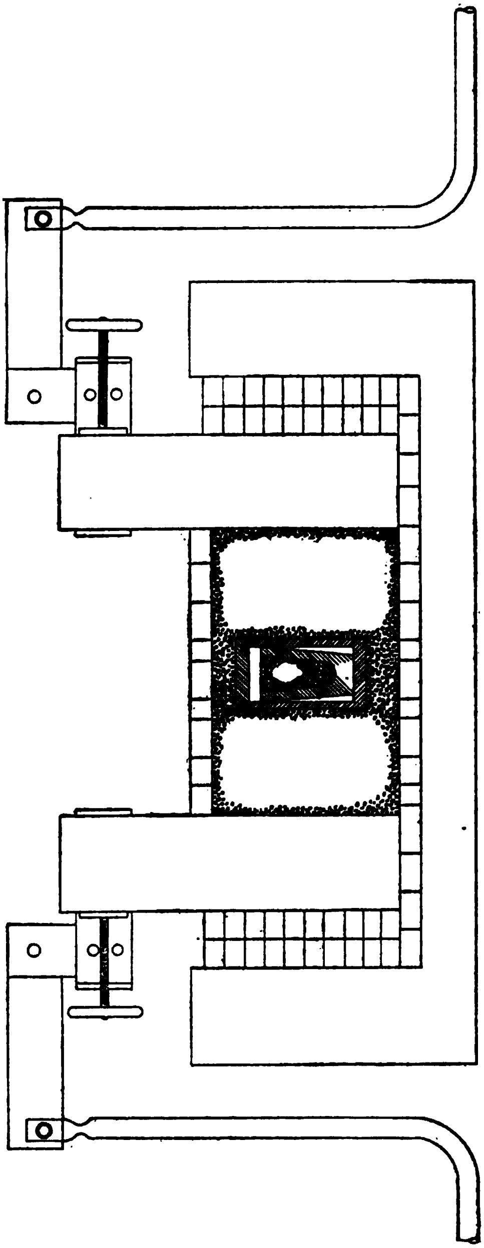


FIG. 5.—*Kryptol furnace with crucible in position*

large-scale operations, owing to the relatively smaller surface exposed compared with the weight of metal being handled; (2) additions, such as ferroalloys, aluminum, or titanium for purification of the melt, as used commercially, are not permissible in an investigation of this kind; (3) the use of slags for protection from the products of combustion or for eliminating impurities and controlling composition in desired ways is excluded. The importance of the conditions for melting pure iron and its alloys to secure products of very high purity does not seem to have been recognized sufficiently in the past, and we shall therefore give full details of our methods.

1. FURNACES

(*a*) ELECTRIC FURNACES.—For ease and convenience of manipulation a furnace used for melting pure iron should maintain continuously a temperature of not less than 1600°. The temperature required eliminates furnaces wound with nickel or nichrome; molybdenum or platinum-wound furnaces are not desirable for work in high vacua, owing to volatilization of these metals with resulting contamination of the melt and destruction of the heater. Tungsten windings could no doubt be used, but no suitable furnace of this type was available at the Bureau. Our work with electric furnaces has been confined, therefore, to those employing carbon in some form as resistor. A furnace of the kryptol type, shown in Fig. 5, was constructed and has been found satisfactory. The Arsem vacuum furnace, shown in Fig. 6, was extensively used and is very suitable for work of this character. As this furnace has been described elsewhere[4] we omit details here. The Helberger crucible furnace was used for melting some of our alloys. This furnace is intended to be used with conducting crucibles, but our work was done with amorphous carbon tubes as resistors. Because of the lack of protection of these from the oxidizing action of the air their life is incon-

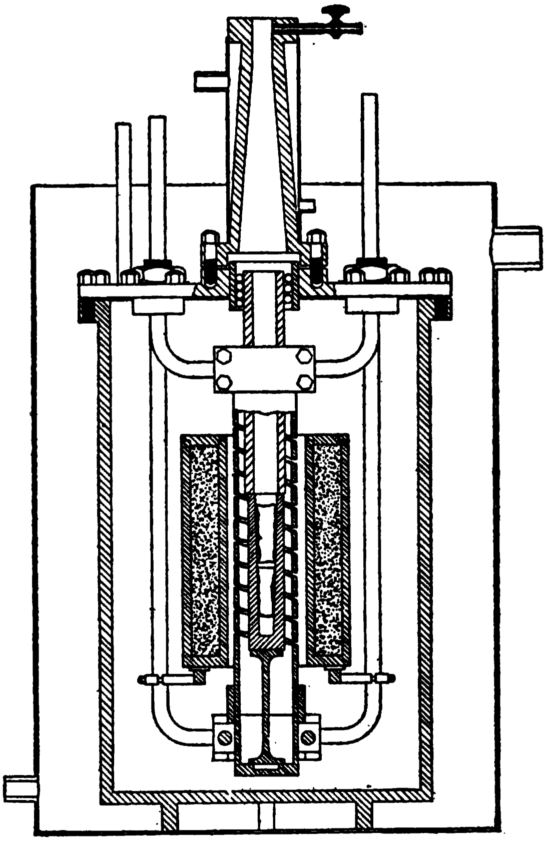


Fig. 6.—*Arsem furnace with crucible and protecting tube in place*

veniently short. The resistance of Acheson graphite tubes was found to be too low to permit the desired temperatures to be reached. There were difficulties in securing good electrical contact between the terminals and the resistor so that this style of furnace as used by us is not to be recommended for work at 1600° or above. The difficulty common to all the types of electric furnaces used (unless the precautions mentioned later were observed) was that the melts were contaminated by volatile sulphur, silicon, or carbon derived from the resistors used. This contamination was least in the Arsem furnace when protecting the crucible, as shown in Fig. 6, and was greatest in the Helberger furnace and in the kryptol furnace when using amorphous carbon as resistors.

---

[4] W. C. Arsem, Trans. Am. Electrochem. Soc., 9, p. 152; 1906.

TABLE 3

Analyses of Bureau of Standards Electrolytic Iron after Melting in Various Furnaces

Manner of melting	C	Si	S	Mn	P	Cu
	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Original iron not melted	0.004	0.001	0.004	Trace	Trace	....
In kryptol furnace filled with Acheson graphite	.012	.01	.004	Trace	Trace	....
In Helberger furnace	....	.014	.024	Trace	Trace	....
In Arsem furnace	.010	.007	.007	Trace	Trace	0.012
In Helberger furnace and remelted in Arsem furnace	.009	.004	.005	Trace	Trace	....
In gas furnace	.012	.003	.02	Trace	Trace	....

Table 3 shows the amounts of contamination introduced by melting pure iron in various types of furnaces. An analysis of the amorphous carbon used as filling material in the kryptol furnace and for the resistor tubes of the Helberger furnace showed 0.75 per cent sulphur and 0.07 per cent silica. The high sulphur in the amorphous carbon resistors is due to the use of petroleum coke in their manufacture. Analyses of best grades of petroleum coke obtained by the Geological Survey showed percentages of sulphur ranging from 0.63 to 1.37 per cent. After having discovered these defects in amorphous carbon we discontinued its use, employing granular Acheson graphite of the best grade for the kryptol furnace and a graphite spiral for the Arsem furnace. A resistor from the Arsem furnace contained

0.02 per cent sulphur and 0.03 per cent silica. The results were satisfactory. It may be concluded that if carbon resistance furnaces are intended for making melts with minimum contamination by volatile substances from the heating element, the best material available at present is first-quality graphite; and that the resistors should be carefully analyzed to insure against impurity before installing them in the furnace. It is further evident that if the refractory walls of the furnace are in immediate contact with the heater, the former should be made of material not likely to react with the heated carbon. Such reaction would cause not only possible contamination of the melt, but also irregularities in the working of the furnace. For this reason ordinary fire clay or silica bricks, or any others containing silica in considerable amount, are excluded. In our own kryptol furnace commercial magnesite bricks were used, and while they were not all that could be desired they proved serviceable, provided the resistor was renewed occasionally.

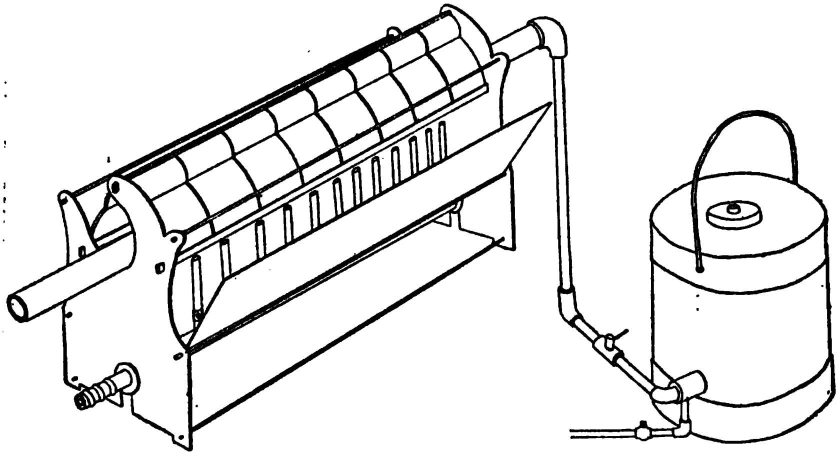


FIG. 7—*Small gas furnace with preheater*

(*b*) GAS FURNACES.—Two types of gas furnace, shown in Figs. 7 and 8, were used and no difficulty was experienced in maintaining the necessary temperatures. The furnace shown in Fig. 7 was a standard type except in respect to the blowpipe, which is similar to that used in tool forges, or for brazing purposes.

A preheater raised the temperature of the necessary volume of air to about 350°. In some experiments made with this furnace pure platinum wire was melted, indicating that a temperature in excess of 1750° had been attained. The refractory lining supplied by the manufacturers was found to have a very short life under these conditions, so that we later covered it with alundum cement, or with a mixture of alundum cement and clay, which prolonged the life. The surface combustion furnace (Fig. 8) proved to be very suitable. This furnace has already been illustrated and briefly described.[5] The same trouble was experienced with the original refractory lining, and repairs were again made with alundum and clay. The highest temperature

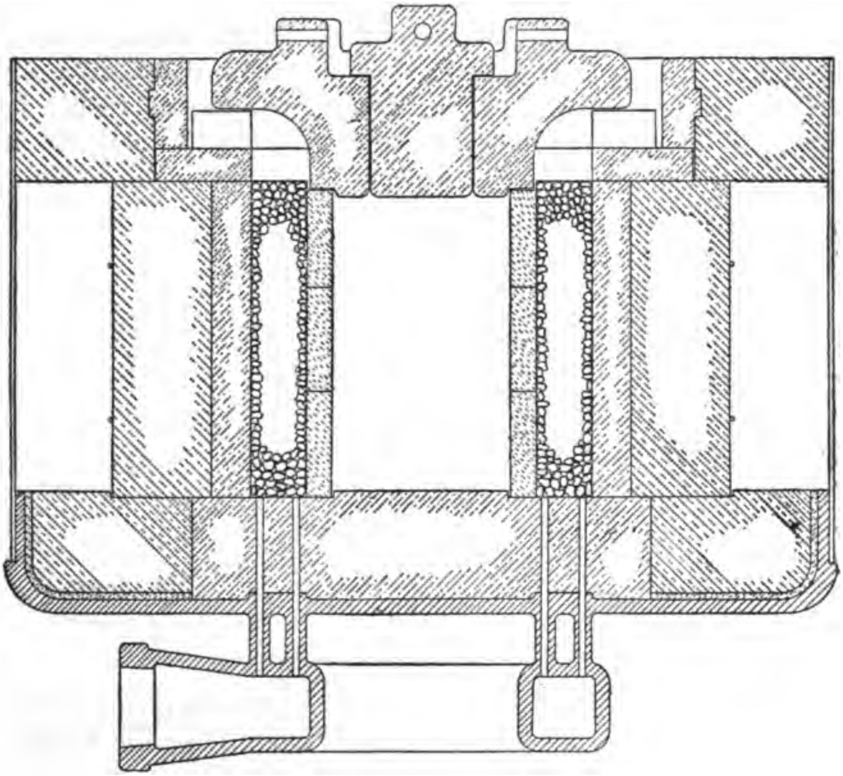


Fig. 8—*Surface combustion crucible furnace*

reached in this furnace, 1670°, was obtained when burning about 180 cubic feet of city gas per hour. In using this type of furnace for pure melts, the crucible must be protected from the large amount of very fine dust blown out of the contact material during operation.

---

[5] Lucke, J. Ind. and Eng. Chem., 5, p. 801; 1913.

2. CRUCIBLES

A few preliminary experiments with clay crucibles showed that it would be out of the question to use these for melting pure iron-carbon alloys. The clays used for making the crucibles which we tried were not sufficiently refractory and were badly corroded by the iron oxide which coats the surface of all melts made in gas-fired furnaces. This did not occur in the electric furnaces, but here the reducing atmosphere, which prevented oxidation, also caused the introduction of relatively large amounts of silicon from the clay. Alundum crucibles were tried, but gave the same trouble as those of clay. Crucibles made of electrically fused or sintered magnesia from two different sources were given a trial in the various types of furnaces, but with these also there was more contamination of the melts by silicon than seemed desirable. (See Table 4.)

TABLE 4

Alloys Made in Crucibles of Commercially Pure Magnesia

Designation	Method of melting	C	Si	S
		Per cent	Per cent	Per cent
P 27	Gas and vacuum furnaces	0.584	0.056	0.004
P 28	do	.022	.029	.030
P 29	do	.367	.015	.029
P 41	Single melt in Helberger furnace	.886	.024	.013
P 39	Melted twice in Helberger furnace	.688	.054	.026
P 31	Helberger and vacuum furnaces	.210	.032	.020
P 32	do	.252	.022	.010
P 33	do	.094	.041	.024
P 35	do	.146	.050	.029
P 37	do	.088	.050	.039
P 40	do	.765	.033	.015
P 42	do	.058	.070	.016
P 36	Melted twice in kryptol furnace	.927	.045	.019

As it had become evident that the desired results could not be secured with any kind of crucible on the market, we began the experiment of making our crucibles of various grades of chemically pure magnesia calcined in the electric furnace at 1600° to 1800°. Although our product contained usually not over 0.05 to 0.10 per cent silica the alloys melted in crucibles made from such magnesia still carried too much silicon. (See Table 4.) Because of the difficulty of securing from chemical dealers magnesia sufficiently low in silica, the high cost of a good grade of this material, and the need of large quantities for several contemplated investigations, we decided to prepare our own material. An endeavor was made to develop a method free from too many complicated manipulations. As raw material we used two or three grades of pharmaceutical manesium carbonate carrying 0.1 or 0.2 per cent silica, and later a calcined Grecian magnesite with about 3.5 per cent silica. Attempts to prepare silica-free magnesia from these sources by dissolving them in hydrochloric acid, evaporating the solutions to dryness and baking, followed by solution of the $MgCl_2$, filtration and precipitation of magnesium carbonate by ammonium carbonate were not very successful on the scale tried, for the technique was difficult and the product unsatisfactory, as well as expensive.

TABLE 5

Percentage of Silica in Magnesia from Different Sources

Source	SiO_2	Source	SiO_2
	Per cent		Per cent
Calcined Grecian magnesite	3.15	Bureau of Standards MgO, prepared from acetate	0.008
Do	4.61	Bureau of Standards MgO calcined in gas furnace	.013
University of Illinois electrically calcined MgO	1.99	Do	.017
Magnesium aluminate tube	5.39	Crucible made from Bureau of Standards calcined MgO	.025
MgO reagent (uncalcined) A	.03		
MgO reagent (uncalcined) B	.07		

After trials of several other methods we developed the following procedure, which has produced a magnesium oxide carrying usually not over 0.01 per cent silica, and at low cost.

The Grecian magnesite was dissolved in commercial acetic acid (70 per cent), using a slight excess of the latter; more of the magnesite was then added until the solution was alkaline to litmus paper, after which the solution was diluted with about twice its volume of water, the whole thoroughly stirred and allowed to stand in barrels for a day or two; at the end of this time the clear solution was siphoned off into a large wrought-iron basin and rapidly evaporated over a large Fletcher burner, adding fresh liquid at intervals until a sufficient amount of the magnesium acetate had separated. The evaporation was then carried to the point where the solution solidified on cooling, after which the decomposition of the acetate into oxide was effected by directing the flame from a large Teclu burner over the surface of the separated salts. The magnesium oxide so obtained is contaminated by carbon, undecomposed acetate, and a little iron, but after calcining is quite suitable for use in making crucibles. The calcining was done in large gas furnaces which gave a temperature of approximately 1550°. The magnesia, as taken from the iron basin, was moistened slightly with water and made up into large balls, which were placed inside an ordinary No. 20 plumbago crucible coated on the inside with alundum cement, or lined with an Acheson graphite crucible. The crucible was carefully covered during the calcining operation, which lasted about two hours. As a result of this treatment the magnesia had shrunk to about one-third its original volume, all the carbon had burned out, and the silica content was very slightly increased. We found it important to blow air through the furnace for several minutes after shutting off the gas, in order to remove the last traces of products of combustion carrying sulphur. If these are allowed to remain in the furnace during the cooling period, the magnesia takes up some sulphur; our best material contained less than 0.01 per cent of this element. Calcining in the gas furnace at the temperature named gives a product which still shrinks a little when used in crucibles heated to higher temperatures, but we had no serious trouble with crucible failures on this account.

Two sizes of crucibles were used which, together with the molds employed for making them, are shown in Fig. 9. The calcined material was mixed with about 10 per cent by weight of uncalcined magnesia and the whole wet with water until it formed a pasty mass. The thin brass cups used for lining the molds were put in place and there was introduced into the mold a sufficient amount of the material (ascertained by preliminary trials); a pressure of 5000 to 10 000 pounds per square inch was applied to the head of the plunger and kept there a minute or two after the plunger had been driven down as far as it would go. The mold was then opened by removing the rings, the brass cup carrying the crucible removed, and the plunger taken out. The crucibles were dried at 100° to 120° for a day and the brass cups stripped off by melting the solder from the joints. They were then either used directly for melts, or after heating to 1200° to 1600° in a gas or electric furnace. The latter procedure is necessary for all crucibles that are to be used in vacuum furnaces.

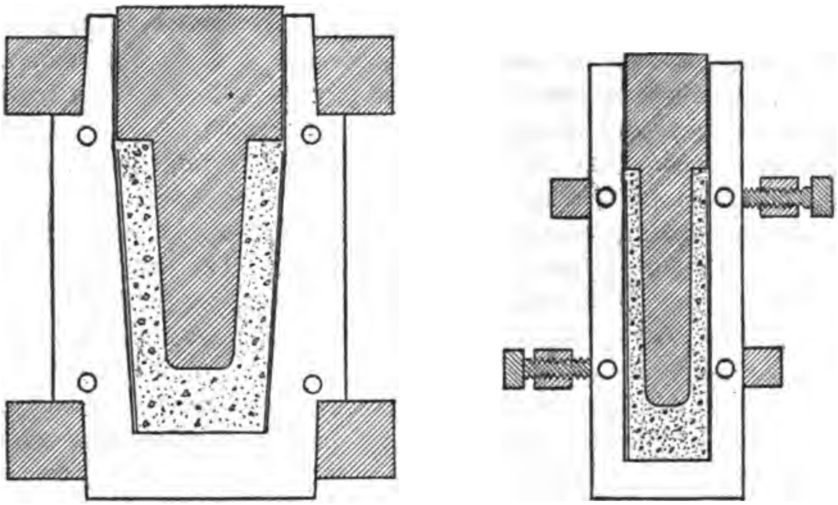


FIG. 9.—*Crucible molds*

IV. PROCEDURE IN MAKING ALLOYS

We first attempted to make ingots in the following manner: The iron as stripped from the cathodes was dried, broken into small pieces, and placed in the larger magnesia crucibles (Fig. 9), together with a suitable quantity of carbon. These were brought gradually to temperatures above the melting point of iron and left in the furnace for 10 or 15 minutes. After cooling, the crucibles were removed and broken away from the ingots. This procedure, while apparently wasteful, was necessary for several reasons: (1) Magnesia crucibles are extremely fragile at high temperatures and any attempt to handle them results in breakage with resultant loss of melts; (2) with the small mass of metal which we used (100 g) it would be impossible to pour successfully; and (3) even if it could be accomplished, pouring would be objectionable because of the added danger of contamination. Moreover, the loss of the crucible is not serious, since the material can be recovered and worked up into new crucibles repeatedly.

The ingots obtained in the manner above described were found to be very unsound and full of blowholes; in this respect there was little difference between those made in the various furnaces. This seemed surprising in view of the difference in atmosphere over the melt in a gas furnace, where the conditions are oxidizing to iron, and in an electric furnace, where carbon dioxide, water vapor, or oxygen—the gases which would oxidize iron at high temperatures—are present only in very small amounts. It would thus appear that the blowholes in iron may be caused by carbon monoxide as well as by any or all of the other gases named, and that the maintenance of a reducing atmosphere is no guarantee of freedom from blowholes. That the melts made in the kryptol furnace were made under reducing conditions is evident from Fig. 5, which shows that the crucibles are completely covered with carbon at all times; this is further evident from an oxygen determination made on drillings from an ingot melted in the kryptol furnace. The percentage of oxygen in this ingot, notwithstanding the fact that no deoxidizer had been used, was 0.03.[6] The weight of these ingots was about 100 g. Fig. 10 (*a*) is a photograph of a split ingot, showing the unsound structure.

The introduction of a regulated amount of carbon into the alloys gave a good deal of trouble. In the gas furnace the amount of oxidizing gases was so great, relative to the weight of carbon introduced, that the latter was all burned out before the melting operation was completed, even when special precautions were taken to protect the crucibles. These difficulties were finally overcome by using the following procedure, which has been fairly satisfactory: The electrolytic iron was first melted down in the larger crucibles in a gas or electric furnace. The ingots of pure iron so made were sawed into longitudinal strips of convenient size for insertion into the smaller magnesia crucibles (Fig. 9) and the necessary amount of carbon was added. The crucible was placed in the vacuum furnace with the protecting chimney in place, as shown in Fig. 6. The furnace was evacuated to 0.2 mm, and the current through the heater was increased gradually until the iron had melted and dissolved the carbon; this point was determined by observation through the window. As soon as this stage was reached a violent ebullition took place; sometimes the contents of the crucible were ejected. We attribute this principally to the expulsion of gases from the cavities in the ingots. In 10 or 15 minutes the surface of the melt became quiescent and the operation was ended. After cooling, the ingots were removed by breaking the crucibles.

---

[6] We are indebted to J. A. Aupperle, metallurgist of the American Rolling Mill Co., for this analysis.

Fig. 10*b* shows the sound structure of these ingots, which were usually entirely or nearly free from blowholes. After discarding the surface down to clean metal, the ingots were turned down to the size required for the thermal test specimens (Fig. 10*c*), retaining the chips for analysis. Complete analyses of typical samples are given in Table 6. For comparison, Table 7 is given, showing the results of attempts by two earlier workers to make pure iron-carbon alloys.

We are now building a larger vacuum furnace for producing large ingots of pure iron and iron-carbon alloys, which will be examined either as made or after forging, rolling, and application of heat treatment as to physical properties, magnetic and electrical characteristics, resistance to corrosion, and related properties. Reports of progress in this work will be issued as they are justified. Later we shall deal with the effect of alloying elements other than carbon on the properties of iron.

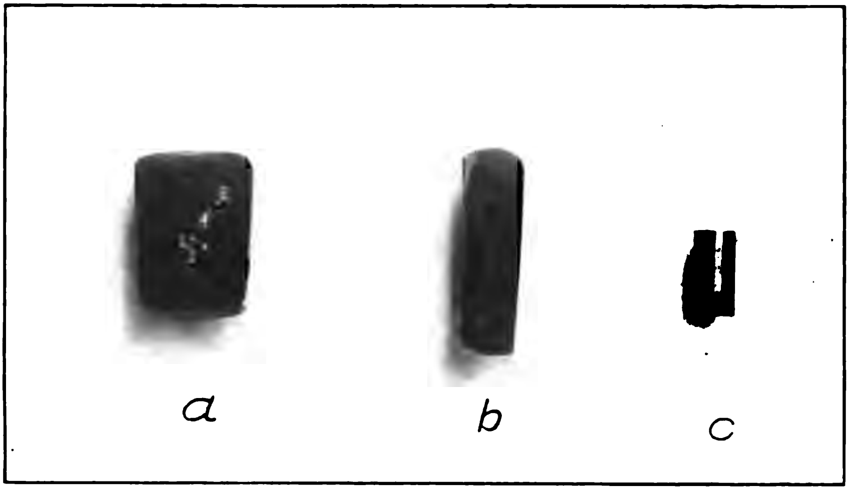


Fig. 10.—*Split ingots and test specimen*

TABLE 6

Analyses of Typical Bureau of Standards Iron-Carbon Alloys

C	Si	S	P	Mn	Cu	Ni and Co	Total Impurities
Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
0.084	0.007	0.009	Trace	Trace	0.020	[a] 0.011	0.047
.376	.013	.009	Trace	Trace	.005	[a] 0.11	.038
.395	.008	.013	Trace	Trace	.012	[a] .011	.044
.597	.010	.008	Trace	Trace	.004	[a] .011	.033
.624	.004	.010	Trace	Trace	.008	[a] .011	.033
.692	.006	.011	Trace	Trace	.008	[a] .011	.036
.860	.006	.006	Trace	Trace	.007	[a] .011	.030
1.087	.006	.006	Trace	Trace	.013	[a] .011	.036
1.797	.010	.005	Trace	Trace	.018	[a] .011	.044
2.240	.005	.005	Trace	Trace	.020	[a] .011	.041
2.560	.005	.005	Trace	Trace	.014	[a] .011	.035
3.27	.006	.006	Trace	Trace	.016	[a] .011	.039

[a] The figures given for nickel and cobalt do not represent individual determinations for each specimen, since the amount of sample was insufficient to allow of these being carried out. Four representative analyses on pure iron and iron-carbon alloys having given the result indicated, it was assumed that these elements were present in that amount in all the samples.

TABLE 7

Degree of Contamination of Iron Melts Made by Others

	C	Si	P	S	Mn
	Per cent	Per cent	Per cent	Per cent	Per cent
Müller's electrolytic iron	0.0630	0.0053	0.0045	0.0024	0.0090
Müller's electrolytic iron after remelting in vacuo in "pure MgO crucible" [a]	.017	.089	.028	.037	.025
C. F. Burgess' electrolytic iron	.009	.006	<.001	.010	Trace
C. F. Burgess' electrolytic iron melted with sugar carbon in magnesia crucible by Howe [b]	2.954	.040	.050	.035	None

[a] A. Müller, Metallurgie, 6, p. 159; 1909.

[b] Howe, Bull. Am. Inst. Min. Eng., p. 1118; 1913, No. 1.

V. DISCUSSION OF THE SOURCES OF CONTAMINATION

1. SILICON

In our earlier experiments, where we were obliged to make crucibles of magnesia higher in silica than that produced by the acetate method already described, we noted that occasionally an alloy of very low silicon content would result from a melt made in a crucible relatively high in silica. The use of our purified magnesia had eliminated all trouble from silicon contamination of melts, but we later decided to make some experiments to determine the relationship between the introduction of silicon and temperature of melting. For this purpose a series of runs was made in the vacuum furnace varying independently the temperature of melting and the silica content of crucibles. One per cent of carbon was added to all these melts since in the presence of carbon there is additional likelihood of contamination due to reduction of silica at high temperatures. The results in Table 8 show that if the temperature is not allowed to rise much above 1600°, crucibles containing as much as 0.9 per cent silica may be used safely. This is of importance when a great deal of work is being done, for it enables one to use repeatedly old crucible material until the silica becomes dangerously high.

TABLE 8

Factors Governing Contamination of Melts by Silicon

Temperature of melting (degrees)	SiO_2 in crucible	Si in melt	Temperature of melting (degrees)	SiO_2 in crucible	Si in melt
	Per cent	Per cent		Per cent	Per cent
1610	0.57	0.007	1720	1.27	0.040
1610	.67	.007	1780	1.20	.042
1610	.75	.007	1770	.19	.007
1610	.91	.006	1720	.24	006
1610	1.14	.015	1760	.31	.021
1610	1.66	.023	1740	.60	.031
1650	1.35	.032			

2. SULPHUR

As has been shown, contamination by sulphur may result from the use of gas furnaces or of petroleum coke carbon in electric furnaces. On abandoning the use of gas furnaces and employing Acheson graphite as resistor material this difficulty disappeared, as is apparent from a comparison of Tables 5 and 7.

3. MANGANESE AND PHOSPHORUS

Both these elements have been reduced to mere traces (less than 0.001 per cent) in all our alloys.

4. COPPER

This impurity, one of the most difficult to guard against, is present in objectionable quantities in some of our melts and to some extent in all. The ingot iron used for anodes contains copper which is not completely removed in the electrolytic refining process, so that our deposits contain about 0.005 per cent of this element. This Cu persists through the melting operation, and unless great care is taken, more is introduced owing to the use of copper connections in furnaces. In particular, the copper blocks used in the vacuum furnace must be smooth and make good contact with the graphite heater, since any arcing causes the vaporization of considerable quantities of Cu with resulting contamination of the melt.

5. NICKEL AND COBALT

Our anode iron contains 0.02 per cent Ni + Co; in the electrolytic refining this is reduced to 0.01 per cent which persists through the melting operations.

6. MAGNESIUM

As all our melting was done in magnesia crucibles it was thought desirable to look for this element as a possible impurity. Several analyses of ingots made in the regular way showed that Mg was not present in any determinable quantity. A rather interesting result, however, was obtained on analyzing some ingots which had been melted at high temperatures (over 1700°). It was found that these contained appreciable amounts of Mg (from 0.005 to 0.01 per cent). Furthermore, the samples were so brittle that the pieces broke while turning in the lathe. It appears at least possible that there may be a direct connection between the two circumstances, though our present data are not sufficient to justify a definite conclusion to that effect.

7. OXYGEN

Unfortunately, the Bureau is not at present prepared to make accurate oxygen determinations on this class of material, but it is hoped later to publish analyses of some of the alloys for this element, if it is found to be present. In our method of preparation, starting with an ingot already low in oxygen (see p. 17) and carburizing in a vacuum furnace where the carbon monoxide resulting from interaction of oxides or oxygen with carbon would be removed as formed, the deoxidation would tend toward completion, and accordingly the alloys should contain but small residual amounts of oxides and oxygen.

VI. SPECTROSCOPIC EXAMINATION

In order to confirm the results of the chemical analyses for small quantities of impurities, the arc spectra of a number of samples of iron and iron-carbon alloys were studied by Dr. K. Burns [7] of this Bureau, to whom we are indebted for the data given below:

MAGNESIUM.—The spectra fully confirmed the chemical tests. Line 2851.1A showed strong in two samples containing 0.007 and 0.010 per cent mg while it was very faint or absent in unfused irons and in alloys which failed to give magnesium by the chemical method.

SILICON.—Line 2881.5A showed presence of silicon in the alloys, but unfused iron showed no traces.

MANGANESE.—Several manganese lines show in various samples of electrolytic iron that have been melted. These lines are absent from the spectrum of unmelted electrolytic iron. The faintness of the manganese lines as compared with those given by a specimen containing 0.01 per cent of this metal indicate a very low manganese content.

CHROMIUM.—The statements made in regard to manganese also apply to chromium.

COPPER.—Lines 3247.7 and 3274.1A are always present though so faint as to be questionable in unmelted specimens.

NICKEL AND COBALT.—Several nickel and cobalt lines show faintly in the various samples.

In the course of the examination of the arc spectrum of pure iron several faulty identifications have been corrected:

2795.542 ascribed to magnesium is iron;
3369.555 ascribed to nickel is iron and nickel;
3412.347 ascribed to iron is probably cobalt; and
3443.645 ascribed to iron is no doubt cobalt.

No attempt has as yet been made to clear up all the doubtful identifications in the iron spectrum; the above list is given to show the possibilities in this direction which may be realized by means of the use of pure iron.

VII. METHODS OF CHEMICAL ANALYSIS

The analyses recorded in this paper were carried out according to well-known principles with suitable precautions, and the methods are given below merely for reference.

---

[7] For an account of the methods used, c. f. K. Burns, Bull. Bur. Standards, 12, pp. 179–196; 1916.

The chips obtained when making the thermal test specimens were thoroughly mixed before weighing portions for analysis. Chips from high-carbon alloys which contained admixed graphite were finely ground and mixed before weighing.

1. CARBON

Carbon was determined by the barium-carbonate titration method devised by one of the authors.[8] The chips (1 to 5 g) were burned in purified oxygen, passing the products of combustion into a solution of barium hydroxide; the barium carbonate was filtered and washed in an atmosphere free from carbon dioxide (see the original for details of apparatus used), and the barium carbonate was titrated against standard hydrochloric acid, using methyl orange as indicator.

2. SULPHUR

Sulphur was determined by dissolving 5 g of the metal, contained in an appropriate evolution apparatus having all ground-glass connections, in concentrated hydrochloric acid, the gases given off being passed into an ammoniacal solution of hydrogen peroxide. After complete solution of the metal the contents of the evolution flask were boiled for 10 minutes while a slow current of purified hydrogen was passed through the solution. The ammoniacal peroxide solution was transferred to a beaker and boiled a few minutes, then the solution was slightly overneutralized with hydrochloric acid and the sulphur precipitated at boiling temperature as barium sulphate. After digestion for a sufficient length of time the precipitate was filtered, washed, ignited and weighed, and the percentage of sulphur calculated.

3. SILICON

Five to 10 g of metal were dissolved in an Erlenmeyer flask in hydrochloric acid (equal volumes of water and hydrochloric acid of specific gravity 1.20), the solution evaporated to dryness and the flask heated on the hot plate at about 200° for an hour. The residue was digested with hydrochloric acid of the same strength as that used for dissolving, the insoluble matter containing the silica was filtered off, washed with dilute hydrochloric acid and water, ignited in a platinum crucible and weighed, after which the silica was volatilized with hydrofluoric acid and its amount determined from the change in weight of the crucible after again igniting. The results were then calculated to silicon.

---

[8] J. R. Cain, Determination of Carbon in Steel and Iron by the Barium Carbonate Titration Method. Bur. Stand. Technologic Paper No. 33.

4. PHOSPHORUS

The usual method of precipitation as ammonium phosphomolybdate was employed, and the phosphorus estimated by comparing the volume of the precipitate with that produced by treating a standard steel in the same way.

5. MANGANESE

The sodium bismuthate method was used.

6. COPPER

Ten to 20 g of metal were dissolved in a slight excess of hydrochloric or sulphuric acid, and hydrogen sulphide passed into the hot solution until all the copper was precipitated. The precipitate was filtered off, and, after washing the paper carrying it, was transferred to a porcelain crucible, and the whole ignited until all the carbon was burned off. A little potassium bisulphate was added and the copper oxide brought into solution by fusion, following by leaching with water and filtration. The solution was compared with a standard solution colorimetrically, either by the ammonia or ferrocyanide method, or by both.

7. MAGNESIUM

Ten to 20 g of metal were dissolved in aqua regia, the solution evaporated to dryness, and dehydrated. The residue was dissolved in 1 : 1 HCl and silica removed by filtration. The iron was extracted by the ether method. After the removal of the iron, hydrogen sulphide was passed through the solution (acidified with acetic acid) to precipitate copper, etc. Manganese and residual iron were removed from the filtrate by bromine and ammonia and the magnesium was precipitated as magnesium-ammonium phosphate. The accuracy of the above procedure was checked by running duplicates to which small amounts of a magnesium salt had been added.

8. NICKEL AND COBALT

The solution of 10 g in $HNO_3 + HCl$ was evaporated to dryness, dehydrated, taken up with HCl of 1.1 specific gravity, filtered, the filtrate evaporated to a small volume, and the iron removed by the ether method. Copper was precipitated with hydrogen sulphide, and the iron and manganese in the filtrate were precipitated by ammonia and bromine. The filtrate was acidified with acetic acid, and nickel and cobalt were precipitated as sulphides from the boiling solution. The two metals were either weighed as oxides or deposited electrolytically from ammoniacal solution, the two methods giving concordant results. The oxides (or metals) were dissolved in hydrochloric acid, the solution was neutralized, and finally made acid with acetic acid and the cobalt precipitated as $K_3Co(NO_2)_6$. After filtering and igniting this precipitate at a low temperature, the cobalt was dissolved, reprecipitated with hydrogen sulphide, and finally weighed as $CoSO_4$. The nickel was determined by the dimethylglyoxime method in the filtrate from the cobalt. The sum of these determinations checked very closely with the total nickel + cobalt found directly.

VIII. SUMMARY

Methods have been developed for producing laboratory samples of iron-carbon alloys, of a very high degree of purity; sources of contamination of melts and means of eliminating them have been described; a method for producing magnesia of a satisfactory degree of purity for making crucibles to be used in work of this kind has been developed; a procedure for making small ingots, which are sound and free from blowholes, without the use of deoxidizers has been worked out. A series of iron-carbon alloys containing 99.96 per cent of the two elements has been prepared, to serve as a basis for the redetermination of the iron-carbon equilibrium diagram.

WASHINGTON, November 11, 1915.

BIBLIOGRAPHY

PREPARATION OF ELECTROLYTIC IRON

Lenz, J. f. prakt. Chem., **108**, p. 438; 1869.
Cailletet, Comptes Rendus, **80**, p. 319; 1875.
Roberts-Austen, J. Iron and Steel Inst., **1**, p. 71; 1887.
Arnold and Hadfield, Stahl u. Eisen, p. 526; 1894.
Hicks and O'Shea, Electrician, p. 843; 1895.
Winteler, Z. f. Elektrochem., **4**, p. 338; 1898.
Haber, Z. f. Elektrochem., **4**, p. 410; 1898.
Abegg, Stahl u. Eisen, p. 736; 1901 (II).
Skrabal, Z. f. Elektrochem., **10**, p. 749; 1904.
C. F. Burgess and Hambuechen, Trans. Amer. Electrochem. Soc., **5**, p. 201; 1904.
Maximowitsch, Z. f. Elektrochem., **11**, p. 52; 1905.
Ryss and Bogomolny, Z. f. Elektrochem., **12**, p. 697; 1906.
Cowper-Cowles, C. A., **3**, p. 1371; **5**, p. 3013; **8**, p. 3648.
C. F. Burgess and Watts, Trans. Amer. Electrochem. Soc., **9**, p. 229; 1906.
Amberg, Z. f. Elektrochem., **14**, p. 326; 1908.
Kern, Trans. Amer. Electrochem. Soc., **8**, p. 103; 1908.
Müller, Metallurgie, **6**, p. 145; 1909 (contains bibliography).
Pfaff, Z. f. Elektrochem., **16**, p. 217; 1910.
Tucker and Schramm, J. Ind. and Eng. Chem., **2**, p. 237; 1910.
Watts and Li, Trans. Amer. Electrochem. Soc., **25**, p. 529; 1914.
Yensen, University of Illinois Bulletin No. 72, 1914.

COLORIMETRIC DETERMINATION OF ACETYLENE AND ITS APPLICATION TO THE DETERMINATION OF WATER

By E. R. Weaver, Assistant Chemist

CONTENTS

	Page
Introduction	28
PART I.—THE DETERMINATION OF ACETYLENE	
A. Literature	29
B. Preliminary experiments	31
1. Solubility and oxidation of copper carbide	31
2. Composition of solution for precipitating copper carbide	32
3. Choice of a protective colloid	33
4. Choice of a preliminary color standard	34
C. Development of colorimetric method	35
1. Apparatus and method employed	35
(a) Apparatus	35
(b) Preparation of standard acetylene solution	38
2. Factors affecting completeness of absorption and color of colloid	39
(a) Methods of study	39
(b) Results obtained	40
(1) Size of tip and rate of gas flow	40
(2) Composition of absorbing solution	41
(3) Temperature	43
(4) Rate of evolution of acetylene	44
(5) Volume of absorbing solution	44
3. Comparison with color standard	45
(a) Dilution of solution after absorption	45
(b) Preparation and standardization of a color standard	45
D. Determination of acetylene in gas mixtures	53
PART II.—THE DETECTION OF WATER BY THE USE OF THE ACETYLENE-CUPROUS CHLORIDE REACTION	
A. Experiments upon the quantitative determination of water	54
B. Qualitative method by solution of acetylene in an anhydrous solvent	56
1. Preparation of reagents	56
(a) Anhydrous solvents	56
(b) Preparation of cuprous-chloride solutions	58
(c) Removal of acetylene from calcium carbide	60

Page
B. Qualitative method by solution of acetylene in an anhydrous solvent—Con.
  2. Method of making test 60
  3. Blank tests 61
  4. Compounds interfering with the test 61
  5. Sensitiveness of test 63
Summary 63

INTRODUCTION

In the course of the examination of certain carefully purified organic compounds it was found that a simple, quick, and very delicate qualitative test for water, showing approximately the amount present, can be made in the following manner: The substance under examination is placed in contact with calcium carbide in the presence of a solvent for acetylene, and any acetylene formed by the action of water is detected by adding the resultant solution to an ammoniacal solution of cuprous chloride. When alcohol or acetone is used as the solvent for acetylene a clear colloidal solution of an intense-red color is formed. Since this reaction appeared to present possibilities as a direct colorimetric method for the determination of water, an effort was made to apply it for this purpose. The results first obtained were very discordant, and it soon became apparent that a careful examination of all the factors which could affect the result would be necessary before any satisfactory procedure could be devised. The investigation of these factors has resulted in the development of a quick and very sensitive method for the determination of acetylene. The application of this method to the determination of water, especially the determination of very small amounts of water in materials of high purity, which was the primary object of the investigation, has been much less successful. The principal sources of difficulty and error in this determination are pointed out in the section of the paper dealing with the determination of water (p. 54). The simpler qualitative methods which are also described (p. 56) have been found very satisfactory, however.

The development of the method for the determination of acetylene will be described in Part I. All of the work upon the detection and determination of water has been brought together in Part II, although much of this work preceded the development of the colorimetric method for the determination of the gas itself.

Part I.—THE DETERMINATION OF ACETYLENE

A. LITERATURE

The use of an ammoniacal solution of a cuprous salt for the determination of acetylene appears to have been introduced by Berthelot.[1] The reagent was greatly improved for qualitative work and its preparation much simplified by Ilosvay,[2] who prepared solutions of cuprous salts by reducing the corresponding cupric salts with hydroxylamine. Ilosvay's investigation was confined to the preparation of the most sensitive qualitative reagent possible. The formation of a red colloid when a small amount of cuprous chloride is added to a solution of acetylene in water was observed by Kuspert,[3] but no attempt to use the reaction for analytical purposes appears to have been made by him or others.

Before proceeding to make experiments upon a colorimetric method for determining acetylene it was necessary to determine the amount of acetylene used in such experiments by an independent procedure, and Berthelot's method of precipitating copper carbide and determining the copper in the precipitate was chosen. An examination of the papers which have been published describing the method for making this determination, together with those relating to the composition and properties of copper carbide, leaves some doubt as to the precautions which must be taken to insure accuracy. The principal point concerning which there appears to be disagreement is the effect of oxidation upon the composition of the precipitated copper carbide. When freshly precipitated in a reducing solution this compound dissolves readily, and, as shown by Scheiber and Reckleben,[4] completely in hydrochloric acid; but if exposed to the air for any considerable length of time before the addition of hydrochloric acid, a black insoluble residue, a product of partial oxidation of either acetylene or copper carbide, is left behind. If this carbonaceous residue is formed directly from acetylene, or if its formation from copper carbide is accompanied by the formation of soluble copper salts, it is obvious that the results obtained in the determination of acetylene will be too low when it is present. The difficulty of preventing this oxidation is shown by the fact that Keiser's[5] efforts to prepare copper carbide free from this substance were unsuccessful and that several other experimenters seem to have had a similar experience. Keiser regarded the residue as carbon; Scheiber[6] determined its composition as $C_{11}H_8O_2$. While the exact composition of the residue has little significance in connection with the determination of acetylene, its method of formation is important.

---

[1] Compt. rend., **54**, p. 1070; 1862.

[2] Ber., **32**, p. 697; 1899.

[3] Z. anorg. Chem., **34**, pp. 453-454; 1903.

[4] Ber., **44**, p. 221; 1911.

It might be inferred from the experiments of Keiser and those of Soderbaum[7] that at least a part of the residue is formed by the incomplete oxidation of acetylene; in this case, of course, part of the acetylene would be used up and the amount of copper carbide formed would be less than corresponds to the amount of acetylene absorbed. However, Scheiber's determinations of the composition of copper-carbide precipitates containing a considerable amount of insoluble matter showed, within narrow limits, a constant molecular ratio of copper to carbon of 1 : 1. If the insoluble portion was formed directly by the oxidation of acetylene and the remainder of the acetylene had formed Cu_2C_2, the carbon would certainly have been in excess.

If, on the other hand, the large amount of carbonaceous residue sometimes observed is produced by the oxidation of the copper compound, one of two conditions must exist: (1) Either the copper must form some other insoluble compound, in which case the oxidation would not affect the subsequent determination of the copper, or (2) a corresponding amount of soluble copper salts would be formed, which would be removed in washing the precipitate, leading to serious error. Blochman[8] describes copper carbide as being unstable in the air, and Scheiber[9] found that it increases in weight when dried in the air. Erdmann and Makowka[10] state that the washed precipitate may be exposed to the air on a filter for two or three hours and then washed with dilute acetic acid without a trace of copper being dissolved, but if the exposure to the air is continued long enough the following reaction takes place:

$$2\,Cu_2C_2 + H_2O + 4\,O = (CH_3COO)_2Cu + 3CuO$$

---

[5] Am. Chem. J., **14**, p. 285; 1892.

[6] Ber., **41**, p. 3816; 1908.

[7] Ber., **30**, p. 762; 1897.

[8] Ber., **7**, p. 74; 1874.

[9] Z. anal. Ch., **48**, p. 537; 1909.

[10] Z. anal. Ch., **46**, p. 129; 1907.

These authors state that copper carbide is less subject than copper sulphide to oxidation by the air.

In their work on the formation of diacetylenyl Noyes and Tucker[11] found that copper carbide will rapidly reduce a solution of cupric chloride, the probable reaction being indicated by the following equation:

$$2Cu_2C_2 + 2CuCl_2 = C_4Cu_2 + 2Cu_2Cl_2$$

Practically all of the observers of the properties of copper carbide, except Blochmann, who found the compound easily changed in air, seem to have worked with a precipitate produced by the complete precipitation of copper by an excess of acetylene. This was certainly the case in the experiments of Erdmann and Makowka. Keiser found that copper carbide has a strong tendency to occlude substances in solution. If acetylene is occluded in this manner, this fact, together with the reaction of Noyes and Tucker, would fully explain Erdmann and Makowka's observation that no copper is made soluble by a brief exposure to the air, since the copper salts would, at first, be reprecipitated by the occluded acetylene as fast as formed by oxidation. When, however, the precipitate is formed in the presence of an excess of a cuprous salt, the formation of cupric salts would be expected to take place immediately on exposure to the air.

B. PRELIMINARY EXPERIMENTS

1. SOLUBILITY AND OXIDATION OF COPPER CARBIDE

Since the literature on the subject does not make entirely clear the effect of oxidation on the determination of acetylene by this method, it seemed advisable to make a few preliminary experiments before using the method for the determination of acetylene in the standard solutions.

The complete insolubility of copper carbide noted by all observers was first confirmed by precipitating, with an excess of acetylene, a copper-sulphate solution which had been reduced by hydroxylamine. The precipitate was filtered and washed freely with dilute ammonia and with water. No trace of copper could be detected by the use of hydrogen sulphide in either the filtrate or the washings.

---

[11] Am. Chem. J., **19**, p. 123; 1897.

In another experiment a limited amount of acetylene was passed into a cuprous-chloride solution containing hydroxylamine. The precipitate was filtered and then washed with water containing a little ammonia and hydroxylamine without allowing air to come in contact with the precipitate. About 200 cc of wash water was required before the washings showed no trace of copper by the ferrocyanide test. After this the precipitate was further washed with 50 cc of dilute ammonia and then with 50 cc of water in order to remove hydroxylamine. The precipitate was then covered with 50 cc of dilute ammonia of the strength used for washing and air was bubbled through the liquid, portions being drawn off through the filter from time to time and tested for copper. Potassium ferrocyanide gave a positive test for copper almost immediately and in the course of about 15 minutes the liquid was colored distinctly blue by dissolved cupric-ammonium salts. Finally, the liquid was drawn off and the precipitate exposed to the air overnight. When water was added a large amount of cupric salt went into solution at once.

This experiment made it evident that in order to obtain accurate results in the determination of acetylene by the cuprous-chloride method it would be necessary to exclude air during the whole procedure.

In the hope of avoiding the difficulty of excluding air, experiments were made with silver salts as a substitute for cuprous chloride. It was found that the silver in silver carbide can be readily and accurately determined; but the reaction of acetylene with ammoniacal solutions of silver nitrate was found to be so slow that the use of this method was impracticable. The experiments made on this point confirm the conclusions of Rivett.[12]

2. COMPOSITION OF SOLUTION FOR PRECIPITATING COPPER CARBIDE

The experiments with silver nitrate having proven solutions of that salt to be unsuitable for the determination of acetylene, cuprous chloride was used. An absorption apparatus[13] was employed which permitted the filtration and washing of the precipitate without exposure to the air. The inclined tube in which absorption took place was about 60 cm long and the gas bubbles remained in contact with the liquid 8 to 10 seconds.

---

[12] Chem. News, 104, p. 261; 1911.

[13] See Fig. 2 in the article by Weaver and Edwards, J. Ind. Eng. Chem., 7, p. 534; 1915.

A series of experiments of a qualitative nature was made to determine the composition of the absorbing solution which would give the best results. The comparative rates at which hydrogen containing acetylene could be passed through different solutions in the apparatus without showing a trace of acetylene in a second apparatus was one of the tests used; but the most useful criterion of the speed of absorption was the distribution of the precipitate which adhered to the glass in the absorption tube. When using the best absorbing solution practically all of the acetylene was precipitated within 20 cm of the inlet, and the glass beyond that point remained free from precipitate. When absorbing solutions were used which permitted the escape of some of the acetylene into the second wash bottle the precipitate was distributed throughout the length of the absorption tube. The absorbing solutions tested in this way contained varying amounts of cuprous chloride, ammonia, ammonium chloride, and hydroxylamine.

The solution which was found to give the best results was made by adding 1 g of cuprous chloride, 1 g of hydroxylamine hydrochloride, and 10 cc of concentrated ammonium hydroxide to 50 cc of water. When the gas was passed through this solution at a moderate rate no trace of acetylene could be detected at the outlet of the absorption apparatus by passing the gas through more of the same solution. After filtering and washing, the precipitates of copper carbide dissolved completely and rapidly in dilute hydrochloric acid. The amount of acetylene was calculated from the amount of copper present in this solution as determined by one of the usual methods.

3. CHOICE OF A PROTECTIVE COLLOID

In order to keep the copper carbide in the colloidal form and to prevent precipitation with a resultant change of color, it is necessary to add a protective colloid. Gelatine, dextrine, gum arabic, and water glass were tried for this purpose. The gelatine solutions were invariably found to be the most uniform and permanent, confirming the results of Küspert.[14] Consequently, gelatine was used in the preparation of all the solutions used in subsequent work.

---

[14] Z. Anorg. Chem., **34**, p. 453–454; 1903.

4. CHOICE OF A PRELIMINARY COLOR STANDARD

A primary requirement for a colorimetric method is a standard for comparison. Obviously, the most satisfactory standard for use with a colored solution is a solution of the same character having a known value, provided such a standard is sufficiently permanent or readily reproducible; a colloidal solution of copper carbide possesses neither of these requirements. When sealed in a glass tube a solution of the colloid containing a considerable excess of hydroxylamine has been kept for as much as a week without apparent change; but a solution in a sealed tube is not a convenient standard for comparison in a colorimeter. Even though oxygen is wholly excluded, the deep blue color of cupric-ammonium salts will eventually appear in consequence of the reaction $Cu_2Cl_2 = CuCl_2 + Cu$, which takes place quite rapidly in ammoniacal solution. It is also very difficult, if not altogether impossible, to make a sufficiently accurate standard by the use of known amounts of acetylene or of water, since the small amounts required could be measured with sufficient accuracy only in very dilute solution, and dilute solutions of either are very hard to keep without change.

It would be useless to describe in detail the many unsuccessful efforts that were made to obtain a suitable standard. Colloidal solutions of copper ferrocyanide and of copper carbide made by passing an excess of acetylene into dilute solutions of cuprous salts were found unsuitable. After trying a very large number of organic dyes a solution having the following composition was chosen as the most suitable and convenient standard:

Chromanilbraun R	milligram	0.21
Carmoisine B	do	.04
Gum arabic	grams	2.5
Water	cubic centimeters	100.00

This solution was designated on an arbitrary color scale as standard "H 25" and will, for the sake of brevity, be so designated in this paper. Unless the contrary is stated it may be assumed that this solution was used in all the observations which follow. Further experiments with color standards and their evaluation will be described in a later section of this paper (p. 45).

C. DEVELOPMENT OF COLORIMETRIC METHOD

1. APPARATUS AND METHOD EMPLOYED

(a) APPARATUS

A solution of acetylene in ether, measured from an ordinary burette, was used as the source of acetylene. The use of such a solution seemed especially desirable, since it eliminated the variables affecting the amount of acetylene evolved from a constant weight of water when reacting with calcium carbide; and at the same time permitted an exact duplication of the conditions which appeared to be most favorable for the quantitative evolution and determination of acetylene from small amounts of water, i. e., solution in ether with subsequent distillation, in a stream of hydrogen, into the absorbing solution. The results would therefore be applicable in the investigation of the water method itself.

The apparatus used for the purpose is illustrated in Fig. 1. The standard solution of acetylene in ether was contained in the bottle *A* connected, through a siphon, with the lower end of burette *C*. The air drawn into either the burette or bottle to replace the solution used was passed through the wash bottle *B* containing some of the same solution. The stoppers and connecting tubes were sealed in place with paraffin to form air-tight connections.

The acetylene solution was measured from the burette *C* into the flask *D*. The funnel *P* served for the introduction of ether which did not contain acetylene. A stream of hydrogen from the Kipp generator *G* carried the acetylene and ether vapor over into the absorbing solution contained in *E*. *E* was graduated to facilitate the preparation and measurement of the absorbing solution. When the ether in *D* was completely evaporated, the colloidal solution found in *E* was run into the colorimeter tube *F* and compared with the standard contained in another tube not shown in the figure. The depth of solution in the colorimeter was read in the side tube *J*, which was backed by a millimeter scale. The gas outlet tube from *E* was connected with *J* in order that a stream of hydrogen might be used to sweep the bulk of the air out of *F* and thus assist in preventing the oxidation of the cuprous

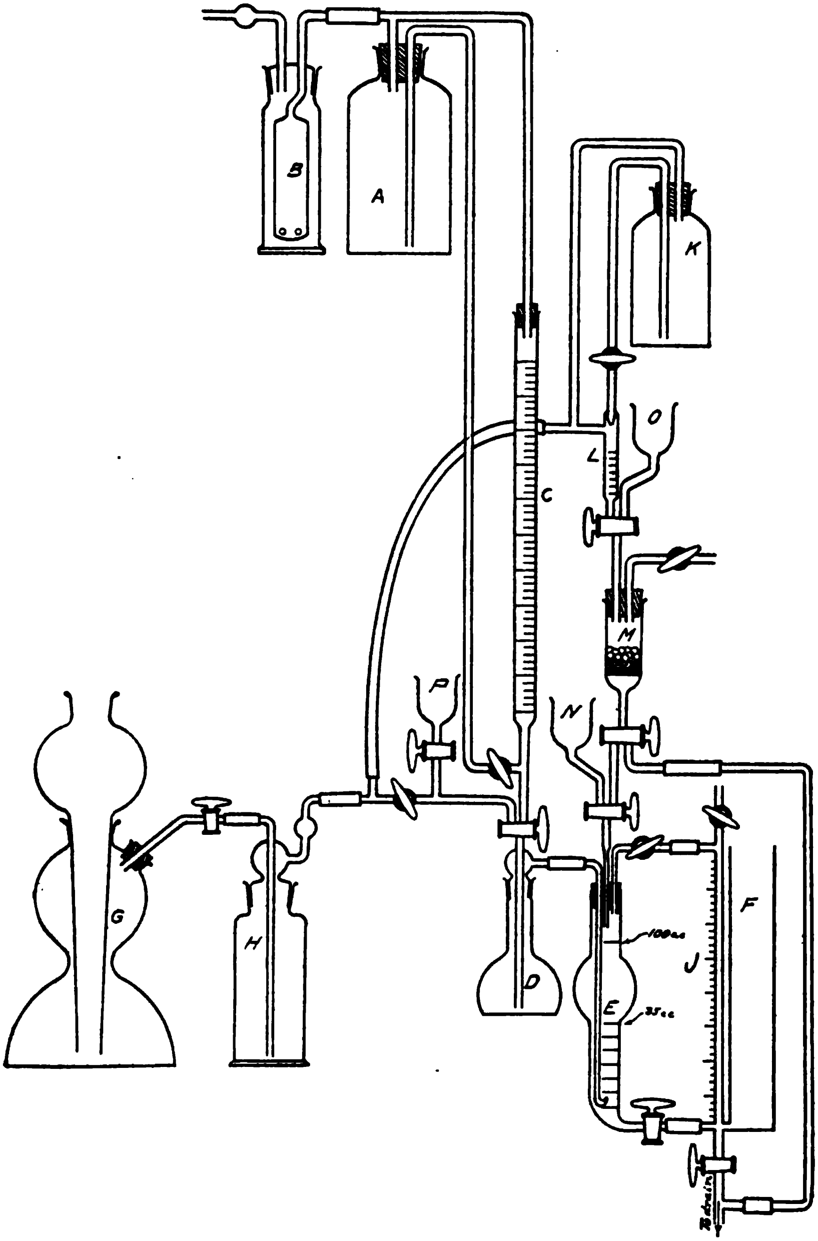


FIG. 1.—*Apparatus used for developing method*

chloride in the colloidal solution. This precaution was found to be unnecessary for any ordinary work, but the arrangement proved very useful when making a large number of comparisons with a single colloidal solution, as in the work with standards described on page 46.

The wash bottle *H* was partially filled, during many of the experiments, with an alkaline solution of pyrogallol to remove any considerable amount of oxygen or acid gases present in the hydrogen used. It served at all times to indicate the rate at which hydrogen was passing and to detect leaks in the connections.

The bottle *K*, containing a hydrochloric-acid solution of cuprous chloride, was protected from access of air by connecting to the hydrogen supply. The solution of cuprous chloride was measured in the graduated tube *L* and run into water contained in *M* which caused the cuprous chloride to precipitate. *M* contained a filter of asbestos resting on a perforated porcelain plate and held in place by a layer of glass beads. The cuprous chloride was filtered and washed, the operation being facilitated by pressure from *G*. After filtration and washing the cuprous chloride in *M* was dissolved through the filter with ammonium hydroxide and run into *E*. The other constituents of the absorbing solution were added through the funnel *N*.

Since an ammoniacal solution of cuprous chloride can not be preserved, owing to the formation of cupric salts with the separation of copper, it was found most convenient to keep the cuprous chloride in hydrochloric-acid solution and to precipitate and wash the salt just before use.

The colorimeter used was of simple construction, resembling that described by Campbell and Hurley.[15] The light from a tungsten lamp was diffused by an opal glass, and reflected from a second opal glass through the comparison tubes to a pair of mirrors set at an angle of 45°. The light is reflected from these mirrors to the eye, producing a divided field.

---

[15] J. Am. Chem. Soc., 33, pp. 1112–1115; 1911.

(b) PREPARATION OF STANDARD ACETYLENE SOLUTION

The standard solution of acetylene in ether was prepared by passing into 500 cc of ether for several minutes a stream of acetylene which had been generated from specially prepared calcium carbide and washed with water. The calcium carbide used was prepared for this purpose by Dr. C. W. Kanolt of this Bureau from pure precipitated calcium carbonate and a considerable excess of sugar charcoal, and was entirely free from sulphur and phosphorus. The acetylene produced had a pleasant odor and produced a pure white precipitate in an ammoniacal solution of a silver salt. The strong acetylene solution thus prepared was diluted with ether to obtain an acetylene concentration convenient for use.

The acetylene in the standard solution was determined from time to time by attaching the absorption apparatus used for the experiment upon the gravimetric method to the outlet of the evolution flask (*D*, Fig. 1), running 10 cc or more of the standard acetylene solution from the burette into the evolution flask, and passing a stream of hydrogen through the apparatus until the ether was entirely evaporated and the apparatus completely swept out with hydrogen. The precipitate was filtered, washed with water containing a small amount of ammonia and hydroxylamine hydrochloride, and dissolved with dilute hydrochloric acid. The copper in the solution was then determined by one of the following well-known methods:

1. The solution was evaporated to dryness and the copper chloride converted to acetate and determined by the iodometric method.
2. The copper was precipitated from hydrochloric-acid solution as sulphide, ignited, and weighed as copper oxide.
3. The chloride was converted to sulphate and the copper determined electrolytically.

Table 1 shows the agreement obtained between duplicate determinations of the acetylene in solution at different times. Many single determinations not shown in the table were made at other times.

TABLE 1

Determination of Acetylene in Standard Solution

Solution used	Date	Volume of solution used	Method for copper	Copper found	C_2H_2 per cubic centimeter of solution
		cc		mg	mg
A	Mar. 15	10	Iodometric	25.5	0.522
		10	.....do	25.8	.528
B	Mar. 27	16	Sulphide	24.7	.315
		10	.....do	15.5	.317
		10	Iodometric	15.4	.315
B	Apr. 18	10	Sulphide	9.8	.200
		10	.....do	10.0	.204
		10	.....do	9.9	.202
B	June 11	10	Electrolytic	5.0	.102
		10	.....do	4.9	.100
		10	Sulphide	5.1	.104
C	July 30	10	Electrolytic	7.8	.159
		10	.....do	7.8	.159

2. FACTORS AFFECTING COMPLETENESS OF ABSORPTION AND COLOR OF COLLOID

(a) METHODS OF STUDY

The influence of the variable factors affecting the formation of the colloidal solution was investigated by absorbing definite amounts of acetylene, from measured volumes of the standard solution, in 30 cc of absorbing solution. After the absorption was completed this solution was diluted to 100 cc before comparing with the color standard in the colorimeter.

The values used for determining the absolute amount of acetylene taken in each experiment were calculated from the results of the last analysis of the standard solution made before and the first analysis made after the experiment in question, on the assumption that the change in concentration of the acetylene solution was uniform during the period. This assumption was certainly not exactly correct, since it was found that the rate of change of the acetylene solution was largely dependent upon temperature changes in the laboratory. However, since it was the purpose of these experiments only to show the effect of a single variable at a time, it was only necessary that the results of each series should be comparable with one another. For this reason the observations of any one series were all made between 9 a. m. and 11 p. m. of a single day, with the exception of one series, which were conducted within a continuous period of 32 hours. In no case was the change in strength of the acetylene solution, during the period covered by a series of tests, sufficient to be detected by the colorimeter.

In each comparison the depth of solution in one tube remained constant while the depth of solution in the second tube was varied until the two appeared to match. This comparison was repeated several times, or as often as necessary to fix the depth of solution required in the second tube within 1 mm.

The results obtained in the 65 tests which were first made, under conditions not subsequently found to cause serious error, were plotted, and a curve was drawn to approximate the average of these results.

Values taken from this curve (called acetylene found) were used to compare the relative amounts of acetylene which would be indicated by tests made under the various conditions. Since only relative values were required, it was not necessary to know the exact position and slope of the curve which would give absolute values. The exact form of the curve fixed by the final series of determinations, made after the effects of all variables had been investigated, is shown in Fig. 5.

(b) RESULTS OBTAINED

(1) SIZE OF TIP AND RATE OF GAS FLOW.—During many of the earlier tests hydrogen carrying acetylene was introduced through a glass tip about 2 mm in diameter. It was evident that absorption was not complete when using this tip, since a ring of red precipitate always formed on the glass at the upper surface of the absorbing liquid. Tests made by passing the gas into a second portion of the absorbing solution always showed the presence of acetylene when any large amount was present in the original sample. A tube with a fine tip about 0.2 mm in diameter, curved

so that bubbles escaping from the tip would pass through the solution without coming in contact with the glass after leaving the tip, was substituted. All subsequent experiments indicated that the absorption of acetylene from the very fine bubbles produced by the use of this tip was practically complete. At the most only a faint trace of red precipitate appeared on the glass at the surface of the solution after several runs, and no color whatever was produced in a second absorption apparatus.

Comparisons of the results obtained by the use of the two tips indicated that, at the rate of flow used for the previous comparisons (about 35 cc of hydrogen per minute), about 30 per cent of the ascetylene had escaped. When the rate of gas flow was increased to 75 cc per minute, while still using the 2 mm tip, the loss of acetylene amounted to more than 50 per cent. When the 0.2 mm tip was substituted, it was found that the results were independent of the rate of gas flow at rates of 5 to 50 cc per minute. Even at a rate of 100 cc per minute the loss amounted to only about 10 per cent.

(2) COMPOSITION OF ABSORBING SOLUTION.—Tests were made to determine the influence of the following constituents in the solution used for absorption: Cupric chloride, ammonium chloride, hydroxylamine hydrochloride, cuprous chloride, ammonia, gelatin, alcohol, and acetone.

The data obtained from the many tests do not, in general, lend themselves to convenient tabulation and plotting, hence only the conclusions drawn from the tests are given here.

In the following discussion of results the amount of each of the various constituents mentioned as present in the solution is always the amount contained in 30 cc.

Cupric Chloride.—It was found that the presence of even quite large amounts of cupric chloride in the absorbing solution is without appreciable effect, provided a sufficient amount of the cuprous salt is also present during the absorption and enough hydroxylamine is added before the colorimetric comparison to reduce all cupric salts. Cupric chloride may be added to a colloidal solution already prepared and left for several hours without affecting the colloid, as shown by colorimetric tests after reducing the cupric salts with hydroxylamine. If the solution is exposed to the air the colloid is unaffected until the cuprous salts in solution are oxidized; then the colloid quickly disappears with the formation of a flocculent black precipitate.

Ammonium Chloride.—The presence of ammonium chloride, or, indeed, any strong electrolyte, causes irregular and generally low results. Ten milligrams of the salt in 30 cc of absorbing solution produced a tendency toward low results. Twenty milligrams caused results averaging 40 per cent low and more than that amount caused precipitation. The presence of ammonium chloride in the absorbing solution is the most serious single source of error in the colorimetric determination of acetylene. After its effect was discovered, solutions showing the characteristic brownish and slightly turbid appearance caused by the presence of much of the salt were discarded.

Hydroxylamine Hydrochloride.—The presence of a small amount of hydroxylamine hydrochloride in excess of that required to decolorize the absorbing solution is without appreciable effect, but a large excess has the same effect as a small amount of ammonium chloride, e. g., 100 mg of hydroxylamine hydrochloride caused average results about 10 per cent low.

Cuprous Chloride.—Only a very small amount of cuprous chloride is required to give complete absorption of the acetylene and the amount present may be varied over a wide range without affecting the results. Solutions containing from 9 to 360 mg gave identical results. Solutions containing 6 mg gave results about 30 per cent low, although the amount of acetylene was much less than equivalent to the amount of copper, while solutions containing only 3 mg of cuprous chloride gave no color at all.

Ammonia.—The amount of ammonia in solution must be regulated rather carefully. About 10 cc of concentrated ammonium hydroxide (specific gravity 0.90) per 30 cc of solution gives the best results. Irregular results are caused by any considerable change in the concentration in either direction. The use of only 5 cc caused results 40 per cent low while the use of 2.5 cc gave results 60 per cent low. More than 10 cc of strong ammonium hydroxide was likely to produce a cloudy appearance caused by coagulation of the gelatin; 20 cc always caused the formation of a large amount of precipitate, sometimes enough to leave the solution practically colorless.

Gelatin.—The amount of gelatin may be varied from 2 to 6 mg per 30 cc provided coagulation does not take place. The amount should be kept small to prevent coagulation. Less than 1 and more than 10 mg are almost certain to cause precipitation.

Alcohol.—The presence of a large amount of alcohol favors uniform results, but alcohol causes gelatin to coagulate and the amount which can be used is limited by this fact. About 10 cc of 95 per cent alcohol per 30 cc of solution gave the most favorable results. When only 5 cc was used the results were about 30 per cent low. Less than 5 cc caused precipitation. Too great a variation of the alcohol concentration in either direction causes precipitation.

Acetone.—The effect of substituting acetone for a part or all of the alcohol was tried. In general, the color of the resulting colloid was changed and comparisons with the standard were difficult. Acetone also coagulates gelatin more readily than alcohol.

Preparation of Best Absorbing Solution.—From a consideration of the above results it is easy to determine approximately the most favorable composition for the absorbing solution. The solution which gives the most uniform results is made up as follows: Dissolve 0.25 g of gelatin in hot water, dilute to 500 cc, and add 500 cc of 95 per cent alcohol and 1.25 g of hydroxylamine hydrochloride. To 20 cc of this solution add 10 cc of concentrated ammonium hydroxide and a small amount of cuprous chloride. One or two hundredths of a gram of this salt is all that is required, although as much as half a gram is unobjectionable. If a greater amount of solution is required to fill the absorption apparatus, it should be made up in the same proportions.

(3) TEMPERATURE.—A few experiments on the effect of temperature were carried out in the same manner as those upon the composition of the absorbing solution. The results show that the temperature changes in the ordinary laboratory would not affect the result appreciably. There was a tendency for the results to be low at temperatures above 35° C. Results at 45° to 50° were 10 to 15 per cent low.

(4) RATE OF EVOLUTION OF ACETYLENE.—In order to test the effect of the rate at which the acetylene is evolved—i. e., whether it is added or produced all at once and passed into the absorber rapidly, or whether it is mixed more uniformly with the hydrogen stream—two methods were used: (1) Varying amounts of ether containing no acetylene were introduced into the evolution flask with the fixed amount of the standard solution; this, in effect, is the same as using a more dilute solution with consequent more gradual evolution of the acetylene; (2) the standard solution was introduced in a number of small portions, each of which was nearly or entirely evaporated before adding the next portion, thus more nearly approximating a uniform evolution of acetylene throughout the experiment. The results of these experiments agreed with one another within 0.01 mg of acetylene when using the small tip, showing that no differences greater than the error of observation were caused by the acetylene being evolved at different rates.

(5) VOLUME OF ABSORBING SOLUTION.—The effect of changing the volume of the absorbing solution is shown in Table 2. In each case the composition of the absorbing solution was the same and the solution was diluted to 100 cc before making the colorimetric comparison. Since these experiments were very carefully made after the effect of all variables had been investigated, the tendency to obtain higher results when using the smaller volume of absorbing solution is probably not due to experimental error. It is believed that this effect is due to equilibrium within the solution, the significance of which will appear later.

TABLE 2

Effect of Volume of Absorbing Solution

Volume of absorbing solution, cubic centimeters	Acetylene taken	Acetylene found	Difference
	Mg	Mg	Mg
30	0.68	0.71	+0.03
30	.41	.41	.0
30	.54	.55	+ .01
30	.27	.26	− .01
60	.41	.38	− .03
60	.54	.53	− .01
60	.27	.24	− .03
90	.41	.38	− .03

3. COMPARISON WITH COLOR STANDARD

(*a*) DILUTION OF SOLUTION AFTER ABSORPTION

A large number of experiments have shown that, within the limit of accuracy of the colorimeter readings, it is immaterial how much the colloidal solution is diluted before the readings are taken, provided the volume of solution is taken into account in calculating the amount of acetylene. For example, if a sample of acetylene is absorbed in 30 cc of solution and the resulting liquid successively diluted with water to 60, 90, and 120 cc and comparisons with the same color standard are made at each dilution, it will be found that the depths of colloidal solution required to match the standard are in the ratios, 1:2:3:4. Some of the results bearing on this point are shown in Fig. 2, and their significance will be pointed out in the discussion of that figure in the following section.

(*b*) PREPARATION AND STANDARDIZATION OF A COLOR STANDARD

After determining the effect of the various factors influencing the color of the colloidal solutions, it was an easy matter to choose a method of procedure which gives uniform results. When using an absorbing solution of the composition already noted (p. 43) it is only necessary to introduce the gas through a fine tip at such a rate as to insure complete absorption; in the apparatus used, a rate of about 35 cc per minute, controlled by counting the bubbles passing through the wash bottle between the hydrogen generator and the evolution flask, was chosen. In order to determine the amount of acetylene in an unknown gas mixture, however, it was first necessary to prepare and determine more accurately the value of a color standard by comparison with colloidal solutions made from known amounts of acetylene by the chosen method of procedure.

Although it is possible to match very closely any depth of a given colloidal copper-carbide solution with a single dye solution, such as solution "H25," described on page 34, the ratio between the depths of the two solutions is not constant, but varies, with the depth. When comparing small depths, the color—i. e., the relative amount of light of the longer and shorter wave lengths transmitted—is the determining factor in making the comparison.

When a greater depth is used, practically all light except red is excluded and the point of agreement is no longer determined by the color of the two fields in the colorimeter, but by whether one field is lighter or darker than the other.

Numerous comparisons have been made which illustrate these effects. Fig. 2 shows the results obtained by matching different depths and dilutions of two colloidal solutions, *A* and *B*, against standard solution "H25." The figure shows the following points of interest:

1. The variation of the ratio between depths of the colloidal and the standard solutions with change in depth of the standard solution, discussed in the last paragraph, is clearly illustrated. If this ratio were constant, the points would, of course, all lie on a straight line passing through the origin.

2. The degree of accuracy of the colorimeter readings is indicated by the agreement of results between different comparisons with the same solution. When using the standard depth (10 cc) of standard solution, the error of a single comparison should not exceed 5 per cent and the average of several readings should give results much closer.

3. The effect of dilution is noted. At the depth commonly used for comparisons (10 cc of standard solution) the agreement between results on the same solution at successive dilutions of 35, 70, and 100 cc is clearly within the limit of accuracy of the colorimeter readings. At greater depth a divergence is apparent.

4. The agreement between duplicates (solutions *A* and *B* were prepared in the same manner from the same amount of standard acetylene solution) is within the limit of accuracy of the colorimeter readings.

Fig. 3 shows the results of comparisons of different depths of a single colloidal solution made from 0.19 mg of acetylene with four different dye solutions which can be used successfully as standards of comparison. Curve *a* represents the comparisons made with a solution of 1 part of azolitmin in 2500 parts of water; curve *b*, with a solution of 1 part of oxamine red in 50 000 parts of water; curve *c*, with a solution made by acidifying with hydrochloric acid a slightly alkaline solution containing 2 per cent of gum arabic and 1 part in 40 000 of oxamine red; and curve *d*,

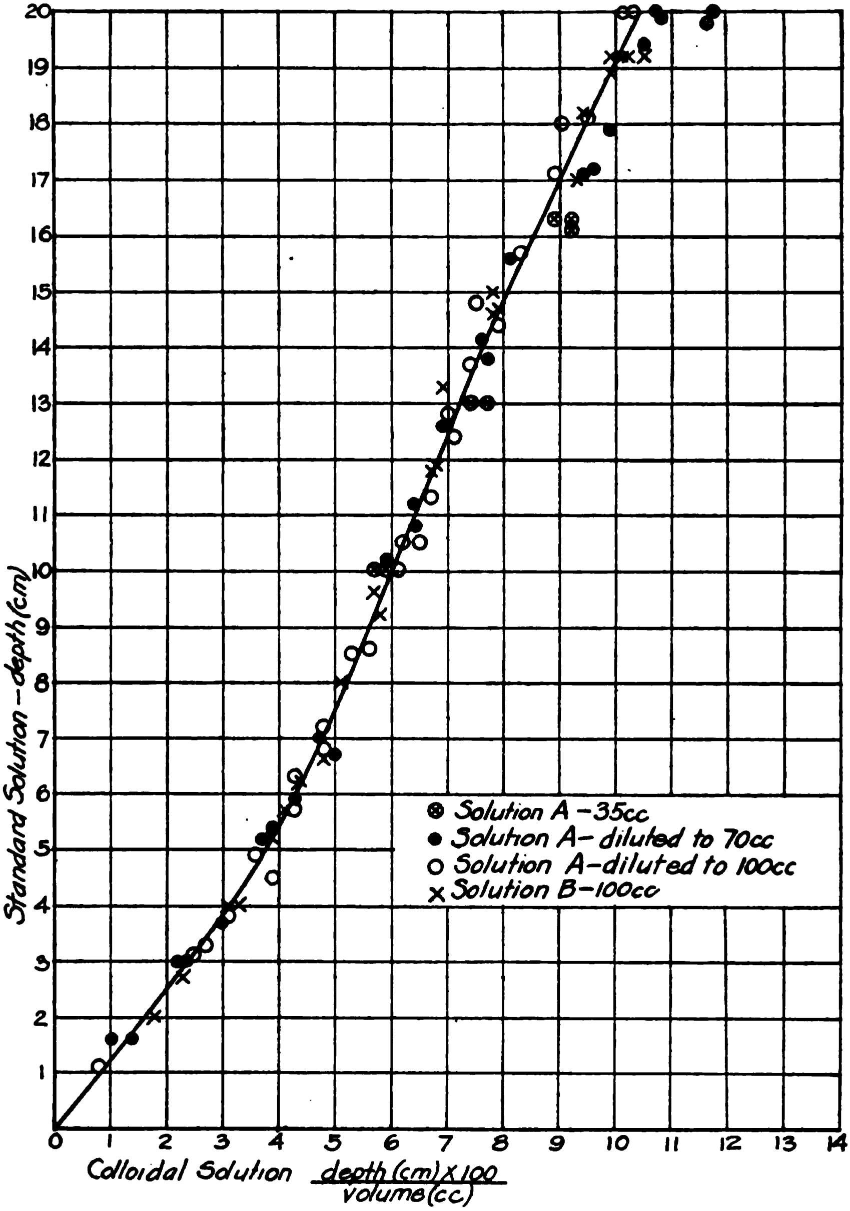


FIG. 2.—*Effect of changing depth of standard solution*

with standard "H25." To avoid confusion, the actual points determined are given for curves *b* and *d* only. The rapid curvature of *a* is due to the fact that azolitmin solutions are almost entirely transparent to red light but screen all other colors even when quite dilute. It will be noted that *d* curves in the direction opposite to the curve in Fig. 2, although made with the same standard solution. This signifies that the character of the two colloidal solutions was not the same. As compared with the standard, the colloidal solution represented in Fig. 3 was relatively more transparent to red than to blue light. The contrary was true with the colloidal solutions in Fig. 2. This was, no doubt, due to the fact that the colloidal particles were larger in

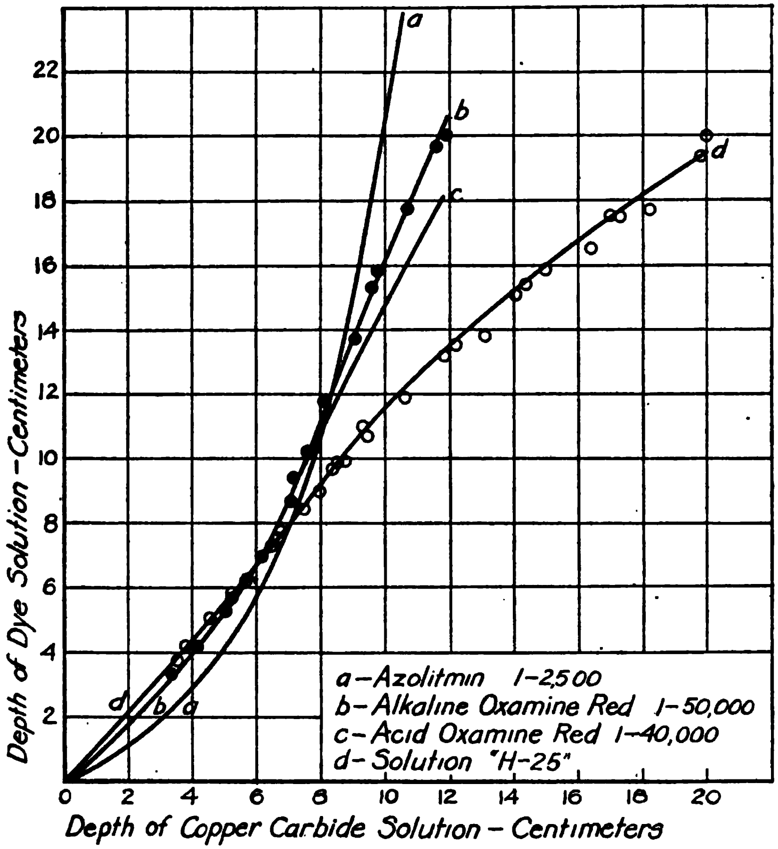


FIG. 3.—*Comparison of color standards*

the latter case than in the former, a condition which may have been caused by the presence of a small amount of ammonium chloride. The transparency to red light decreases rapidly with an increase of the conditions which produce precipitation.

It is evident from a consideration of Figs. 2 and 3 that in order to obtain comparable results it is preferable always to make the comparison of an unknown solution with the same depth of standard solution. In practically all the work described in this paper 10 cm of "solution H25" was used as the standard. When the color of the colloidal solution was so light that the total volume of 100 cc was not sufficient to match 10 cm of the standard (which was the case when prepared from less than about 0.12 mg of acetylene) the whole of the colloidal solution was transferred to the colorimeter and the depth of standard solution varied to match it. The error due to the change in ratio of standard solution to colloidal solution caused by this procedure is always negligible, probably never as much as 0.01 mg of acetylene.

Upon plotting the results of any series of comparisons of the colloidal solutions produced by known amounts of acetylene with a fixed color standard, it appears that within the limits of experimental error the results obtained will all lie on a straight line represented by the equation $x=ay+b$ in which $x=$ amount of acetylene, $y=\frac{1}{\text{depth of colloidal solution}}$ and a and b are constants. In this equation b represents, of course, the point at which the curve cuts the horizontal axis, and its value is that of the smallest amount of acetylene which will produce a color in the absorbing solution. The value of a is dependent upon the color standard used. Both constants must be experimentally determined.

When a variable depth of a standard solution is used for the comparison, the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$ may be used as the value for y and the equation $x=ay+b$ still holds, provided the ratio between the depths of the two solutions is the same for all depths. As pointed out in the preceding section, this is not the case with any of the solutions used as standards, but it may be assumed without appreciable error for amounts of acetylene not greater than 0.1 to 0.2 mg. For larger amounts a constant depth of standard solution should be used in order to provide a color standard of fixed value.

The value of *b* was, at first, thought to represent the minimum concentration of acetylene in the gas mixture which would be absorbed by the solution. If the existence of such a minimum were the true explanation of the fact that the curve does not pass through the origin, it is evident that a given amount of acetylene diluted with a large volume of hydrogen would give lower results than the same amount of acetylene diluted with a small volume of hydrogen. That such is not the case was shown by the experiments described under the heading "Rate of evolution of acetylene" (p. 44). The only other probable explanation seemed to be that there is an equilibrium in the absorbing solution and that *b* represents the minimum concentration of dissolved acetylene which will produce a colored colloid. If this is true, the value of *b* should be proportional to the volume of absorbing solution. The experiments given in Table 3 and plotted in Fig. 4 show that this relation is at least approximately correct.

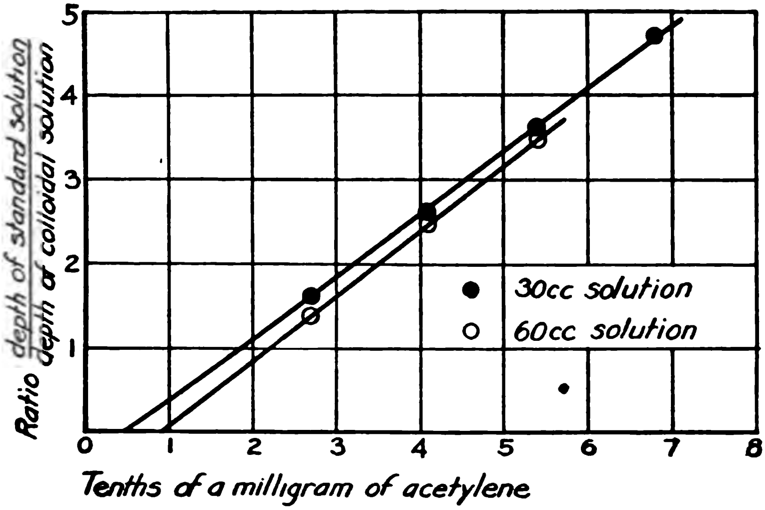


FIG. 4.—*Effect of volume of absorbing solution used*

Fig. 5 shows the results of one series of comparisons of "standard solution H25" with known amounts of acetylene from a carefully analyzed solution in ether. The equation of the straight line averaging these values is $x = 1.43\,y + 0.3$ where x is expressed in tenths of a milligram of acetylene and y is the ratio $\frac{\text{depth of standard solution}}{\text{depth of colloidal solution}}$.

Calibration of any Color Standard.—Since the value of b depends upon the volume of the absorbing solution and is independent of the color standard used, its value may be experimentally fixed once for all. This value has been carefully determined several times under different conditions and has always been found to be between 0.02 and 0.05 mg. It seems probable that in any operations in which there is fairly complete absorption the value of b may be assumed to be 0.03 mg for 30 cc of absorbing solution without causing any error in excess of 0.01 mg. In order to calibrate any color standard it is then only necessary to make one accurate comparison of the standard with a colloidal solution prepared from a known amount of acetylene. This comparison gives simultaneous values for x and y in the equation $x = ay + 0.03$, and the value of a may be easily calculated. Unknown amounts of acetylene may then be determined from the same equation,

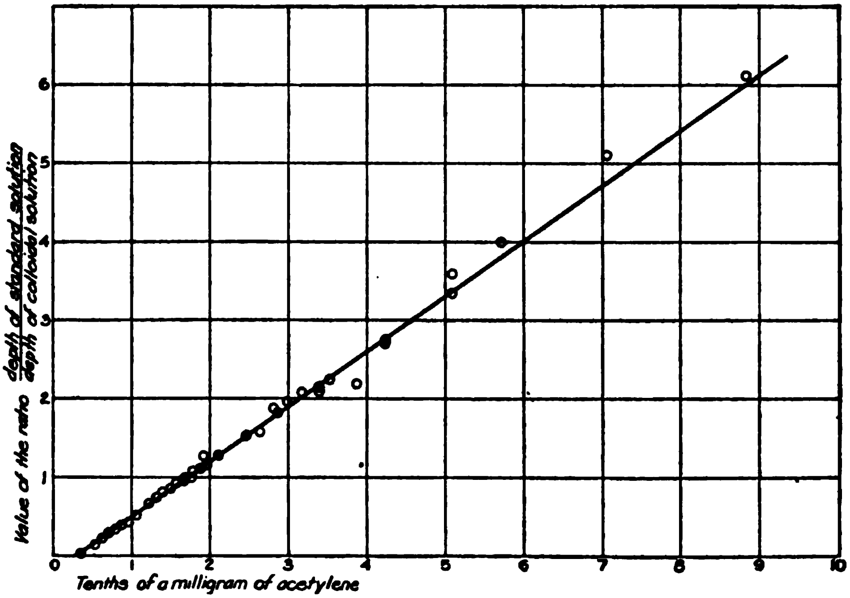


Fig. 5.—*Comparison of standard solution with known amounts of acetylene. Equation of line is* $x=1.43y+0.3$

using the values already found for *a* and *b*, or for convenience a curve may be plotted and values taken from that.

Chemists who desire to make only an approximate determination without the labor of previously calibrating a standard may do so by using as a standard a depth of 10 cm of a solution of 0.04 g of azolitmin in 100 cc of water. The value of *a* for a solution of this strength made from a sample of the dye of Kahlbaum grade was found to be 0.13 mg, *y* representing the ratio between the depth of the two solutions. It is not known how much variation will be found among different samples of azolitmin; but it is apparent from the slope of curve *a* in Fig. 3 that any variation in the strength of the azolitmin solution or the quality of the dye will cause much less than a proportional error in the amount of acetylene found.

As a color standard, a piece of ruby glass or a glass plate covered with a film of gelatin and stained with oxamine red or other suitable dye may be used instead of one of the solutions mentioned on page 46. Once having calibrated the standard as described above, the same results are obtained, no matter what standard is used, provided the two colors are enough alike to permit an accurate comparison and the standard does not change. A ruby glass is, of course, permanent, but the author is unable to say how much reliance may be placed in the permanence of color of a stained film.

Table 3 gives the results of a series of determinations of unknown amounts of acetylene using two different standards for comparison. The results are in substantial agreement.

TABLE 3

Determination of unknown amounts of acetylene, using as standards (1) 10 cm solution H25, a=1.43; (2) ruby glass No. 1, a=3.69

Sample	Acetylene found	
	Solution H25 as standard	Ruby glass as standard
	mg	mg
1	0.51	0.55
2	.43	.41
3	.29	.28
4	.57	.56
5	.56	.55

D. DETERMINATION OF ACETYLENE IN GAS MIXTURES

None of the constituents normally present in illuminating gas interferes in any way with the colorimetric determination of acetylene. To make such a determination it is only necessary to pass a measured volume (0.5 to 2 liters) of the gas into the absorbing solution and make the colorimetric comparison. The whole determination can be made in about 10 minutes. Four successive determinations of the acetylene in illuminating gas taken directly from the house piping gave 0.30, 0.30, 0.32, and 0.33 cc per liter. The method was applied by J. D. Edwards in this laboratory to the testing of hydrogen of high purity. One part of acetylene was readily determined in 250 000 parts of hydrogen from one source. Hydrogen from another source, believed to contain only a small fraction of this amount of acetylene, produced a red stain on the tip of the inlet tube in the absorbing solution, but no coloration in the liquid.

In order to ascertain whether acetylene could be determined in air by this method, a sample of the acetylene solution in ether was first run in the usual manner with a stream of hydrogen to carry it into the absorber; then the determination was repeated, using the same amount of acetylene and a stream of air instead of hydrogen. The acetylene-air mixture was passed through a strongly alkaline solution of pyrogallol and thence into the absorber; and the pyrogallol solution was heated to boiling before the stream of air was stopped. When hydrogen was used the test showed 0.56 mg of acetylene; with air 0.53 mg of acetylene was found. Only one determination was made in air on account of the inconvenience of the apparatus used, but the result showed that acetylene in air can be determined by this method.

The experiment also proved that a solution of potassium hydroxide could be used if necessary to remove hydrogen sulphide, carbon dioxide or similar interfering gases. It was found by several experiments that small amounts of carbon dioxide did not affect the determination, but that larger amounts had the same effect as the introduction of a little ammonium chloride into the solution. The color of the colloid produced by acetylene carried over in a stream of pure carbon dioxide was too brown to admit of any accurate comparison.

Part II.—THE DETECTION OF WATER BY THE USE OF THE ACETYLENE-CUPROUS CHLORIDE REACTION

Calcium carbide has recently been quite extensively used for the determination of water in substances which, for any reason, do not permit the application of the more usual methods of analysis. It was suggested by Berthelot,[16] that the acetylene evolved in the reaction could be determined by absorption in an ammoniacal solution of a silver salt with subsequent titration of the excess of silver. This method was tried by Rivett [17] for the determination of water in butter, but was not successful on account of the incomplete absorption of the evolved acetylene. With this exception, all the chemists who have used the calcium-carbide method seem to have determined the evolved acetylene either volumetrically or by loss in weight. Obviously, neither of these methods is applicable to the detection of very small amounts of water, especially in the presence of other volatile substances.

A. EXPERIMENTS UPON THE QUANTITATIVE DETERMINATION OF WATER

The accurate determination of very small amounts of water by the colorimetric method, which was the primary object of this investigation presents several difficulties which are nearly insurmountable.

Efforts were made to determine water in a variety of materials by the use of the apparatus described below. The sample to be tested was brought into contact with calcium carbide, in a small glass apparatus, either with or without anhydrous ether to act as a solvent. The flask in which the reaction took place was connected to a condenser and thence to a tube filled with carbide to prevent the escape of water vapor. Ether dried over sodium could be introduced directly or could be distilled through a phosphorus pentoxide tube into the reaction flask. The whole apparatus could be swept out with hydrogen dried over phosphorus pentoxide. .

---

[16] Compt. rend., 129, p. 361; 1899.

[17] Chem. News, 104, p. 261; 1911.

The greatest difficulty encountered is due to the fact that calcium carbide itself, or the calcium hydroxide which it always contains, appears to occlude acetylene which it holds with great tenacity but gives off slowly for long periods. It may be that the source of trouble is a small amount of water which is held by the calcium hydroxide and which reacts with the carbide very slowly. Whatever the exact cause, there is no question that with any carbide obtainable commercially all efforts to remove this acetylene by ignition or evacuation have proven unsuccessful. The acetylene which causes the trouble may be removed by boiling the carbide two or three times with an anhydrous liquid such as ether. After such treatment the carbide must not be exposed to the air even for an instant. After the reaction between the carbide and the sample being tested for water is finished, it is necessary to remove the acetylene produced in the same way as before the test. It is apparent that a considerable amount of ether is required for the two purposes and that a large volume of hydrogen is required to sweep out the apparatus completely. It has been found almost impossible to dry ether so thoroughly that the amount required by this test will produce no acetylene which can be detected. Even the ether from a bottle entirely filled with a loose mass of sodium wire, which remains apparently perfectly bright, may produce a surprising amount of acetylene, and phosphorus pentoxide appears to lose very quickly its power to remove the water completely from ether vapor. It is consequently very difficult to secure consistent blanks.

A second source of difficulty, which has been recognized by every chemist who has used the carbide method for the determination of water, is the fact that the calculated amount of acetylene is never produced from a known quantity of water. This is particularly true when dealing with very small amounts of water. In the author's experiments the amount of acetylene produced has varied from 50 to 80 per cent of the calculated amount, generally approaching the latter figure.

In consequence of these sources of difficulty and error, tests made with the colorimeter have little more significance than the much simpler qualitative tests described in the next section. A negative test is quite conclusive, but the detection of an amount of acetylene less than 0.1 mg has little more than qualitative significance.

Negative tests have shown that the standard samples of benzoic acid, naphthalene, and sugar issued by this Bureau are almost absolutely anhydrous. As an example of the kind of results which may be expected when water is present, the following tests are given of a sample of alcohol in which E. C. McKelvy, of this Bureau, had determined the amount of water by the method of critical solution temperature.[18]

TABLE 4

Determination of Water in Alcohol

By critical solution temperature—A. Water found	By carbide method		Ratio $\frac{B}{A}$
	Acetylene produced	B. Water found	
mg.	mg.	mg.	
1.0	0.48	0.62	0.62
1.0	.58	.80	.80
6.0	3.5	4.8	.80
6.0	3.6	5.0	.82
50.0	[a] 21.2	29.2	.59

[a] Acetylene determined gravimetrically.

B. QUALITATIVE METHOD BY SOLUTION OF ACETYLENE IN AN ANHYDROUS SOLVENT

While the quantitative determination of water by reaction with calcium carbide and distillation of the evolved acetylene into an absorbing solution is a complicated, difficult, and unsatisfactory procedure, the detection of water by permitting the reaction with carbide to take place in the presence of a solvent of acetylene, and adding the acetylene solution formed to a cuprous chloride precipitating solution, is rapid, simple, and accurate. The methods found most satisfactory for carrying out this test will now be described.

1. PREPARATION OF REAGENTS

(a) ANHYDROUS SOLVENTS

When testing for water in organic liquids it is usually most convenient to allow the liquid under test to serve as the solvent for acetylene, in which case the previous preparation of an anhydrous solvent is not necessary. In applying the tests to solids, however, it is necessary to allow the reaction with carbide to take place in the presence of an anhydrous liquid, preferably a solvent of the substance under test; and the first difficulty met with in the use of the method was that of preparing even approximately dry solvents. Samples of gasoline, benzene, ether, ethyl acetate, amyl alcohol, amyl acetate, ethyl alcohol, methyl alcohol, acetone, chloroform, carbon tetrachloride, carbon bisulphide, and pyridine were treated with calcium chloride, lime, metallic sodium, metallic calcium, and phosphorus pentoxide, except in those cases where a given drying agent was known to be inapplicable on account of reaction with the solvent. The five solvents first mentioned were thus prepared so nearly free from water that it was impossible to detect a trace of acetylene dissolved in them after several minutes' contact with calcium carbide. Sodium appeared to be the best drying agent for the hydrocarbons and ether, and calcium for the esters. Drying of the other solvents was not carried to completion by the above treatment, but all except pyridine were dried sufficiently to be used successfully as solvents for substances containing any considerable amount of water. The list could, no doubt, be extended almost indefinitely; and nearly all, if not all, of those liquids mentioned could be completely dried by the use of proper drying agents and the observance of suitable precautions. All the liquids tested in this investigation were found to dissolve enough acetylene to give the desired test. Since any of these solvents will, if exposed to the air for a very short time, absorb enough water to show a decisive test, they should be kept, after being dried, in bottles containing some of the drying agent and communicating with the air through a tube containing phosphorus pentoxide. It is difficult to exclude the air sufficiently by the use of ordinary glass, cork, or rubber stoppers unless the pressure differences, due to temperature changes, are eliminated by the use of a drying tube.

---

[18] This Bulletin, 9, p. 344.

The most sensitive tests are obtained when a solvent is employed which is immiscible with water, since the precipitate formed by the subsequent treatment with cuprous-chloride solution, if small in amount, collects at the surface of separation of the two liquids and is very easily detected. If a fairly large amount of acetylene is present, the aqueous layer dissolves enough acetylene to form a precipitate throughout the solution. When the acetylene is dissolved in liquids miscible with water, such as alcohol and acetone, the copper carbide first appears, of course, in the colloidal form, but unless a protective colloid is present it quickly precipitates. Since the precipitate is distributed through a much larger volume when these solvents are used, the test is not nearly so sensitive as with ether or chloroform with which, as above noted, the precipitate is concentrated in a single layer. Furthermore, with some of the miscible solvents, especially with acetone, the precipitation does not appear to be always complete. In fact, it is sometimes possible to discharge the color of a colloidal solution of copper carbide by adding a large excess of acetone.

(b) PREPARATION OF CUPROUS-CHLORIDE SOLUTION

In case alcohol or acetone is used as a solvent and there is no substance present which will precipitate gelatin, it is probably best to use a reagent which will keep the copper carbide in the colloidal form. The following procedure is recommended:

Make up a solution to contain 0.5 g of gelatin and 2.50 g of hydroxylamine hydrochloride per liter. Take a volume of this solution equal to the volume of alcohol or acetone to be tested for acetylene, add an equal volume of concentrated ammonium hydroxide and a small amount (2 to 10 m per cubic centimeter) of cuprous chloride. As soon as the copper salt is dissolved add the solvent to be tested for acetylene.

The composition of the solution containing the colloid is now the same as that found to be the most favorable for the quantitative determination of acetylene, and the amount of acetylene added in solution may be determined, if desired, by a colorimetric comparison.

When solvents are used which are immiscible with water, or when there are substances present which would precipitate gelatin, the copper carbide must be observed in the form of a precipitate, and the composition of the most suitable reagent is somewhat different. When a colloidal solution is desired it is necessary to use a reagent which will prevent precipitation; when a precipitate is to be observed a reagent must be used which will favor precipitation. Ilosvay[19] made a careful study of the composition of the most sensitive reagent for this purpose; he recommends the following proportions for solutions made from several salts:

1. 0.75 g copper chloride ($CuCl_2.3H_2O$), 1.5 g ammonium chloride, 3 cc ammonium hydroxide (20 to 21 per cent NH_3), 3 g hydroxylamine hydrochloride.
2. 1 g copper nitrate ($Cu(NO_3)_2.5H_2O$), 4 cc ammonium hydroxide, 3 g hydroxylamine hydrochloride.
3. 1 g copper sulfate ($CuSO_4.5H_2O$), 4 cc ammonium hydroxide, 3 g hydroxylamine hydrochloride.

In each case the copper salt is dissolved in a small amount of water, the ammonia and hydroxylamine hydrochloride are added, and the solution is diluted to 50 cc. The first of these solutions seems, in general, to give the most satisfactory results. This solution may be used for the detection of acetylene in any of the solvents previously mentioned except carbon bisulphide, which is reduced to hydrogen sulphide by hydroxylamine and precipitates the copper from the solution as a sulphide. When it is necessary to use carbon bisulphide as a solvent the precipitating solution must be made up from cuprous chloride without the use of any reducing agent. It is very difficult to prepare such a solution which is entirely colorless, but a very small precipitate of copper carbide may be readily detected even in a deep-blue solution, and tests have shown that the presence of a cupric salt does not interfere with precipitation, provided a sufficient amount of the cuprous salt is present.

On account of the difficulty caused by the oxidation of cuprous to cupric chloride, experiments were made with a view to replacing the copper solution with an ammoniacal solution of a silver salt; but the white or yellowish precipitate of silver carbide was so much less characteristic and so much harder to detect in small amounts than the red copper carbide that the formation of the latter is the more useful test even when, as in the presence of carbon bisulphide, the copper solution used can not be decolorized.

---

[19] Ber., **32**, p. 697; 1899.

(c) REMOVAL OF ACETYLENE FROM CALCIUM CARBIDE

In order to remove the acetylene (or water) which is always contained in commercial calcium carbide, it is necessary to boil the carbide with one or two portions of the anhydrous solvent, the liquid being completely evaporated before the carbide is used. In case it is not desired to use, for this purpose, the solvent which is subsequently employed in the water determination, anhydrous ether may always be used.

2. METHOD OF MAKING TEST

The test for water is carried out most simply by adding the substance to be tested, together with the solvent, to a few pieces of calcium carbide which have been "boiled out," as described in the preceding paragraph, in a test tube. The test tube is closed by a dry cork or other stopper and shaken occasionally without allowing the liquid to touch the stopper. Two or three minutes' contact with the carbide is usually sufficient. The tube is allowed to stand long enough for the carbide to settle and the clear solvent decanted into the cuprous solution, with which it is vigorously shaken. It might be supposed that small particles of carbide would be carried into the aqueous solution and that the acetylene so produced would make the test of no value; but very little difficulty is experienced from this source. The high density of the carbide causes even very small pieces to settle rapidly, and particles which are carried into the precipitating solution are immediately surrounded by a dense precipitate which causes them to appear as black specks easily distinguished from the bright red, flocculent precipitate produced by dissolved acetylene.

In testing solids, it is preferable to use as a solvent for the acetylene a liquid which also dissolves the solid under examination. This is not absolutely necessary, however, since an anhydrous liquid will generally extract water quite readily from a solid containing it, provided the solid is in a fine state of division. Tests for water in powdered sugar have been made successfully by the use of ether, in which sugar is nearly, if not entirely, insoluble. Tests of nonvolatile acids or other compounds, which it is not desirable to bring into contact with carbide, may be made by adding an anhydrous liquid, which is then distilled off and tested for water, either by passing over carbide in vapor form or in the usual manner after condensation. Gases may be tested by simply passing over carbide, which has been freed from acetylene, and into the cuprous-chloride solution.

3. BLANK TESTS

Whatever procedure is adopted, it is necessary to make a blank test before using the method to detect water in the sample under examination. When testing an organic liquid by simple contact with carbide and decantation, it is only necessary to insure the removal of all acetylene previously held by the carbide. Boiling out two or three times with the liquid under test or with ether, in the manner already described, is always sufficient to accomplish this. Any acetylene found in portions of the liquid subsequently added is due to water in the sample. When using an anhydrous solvent or when distilling in hydrogen it is necessary to make the blank test in the same manner as the test for water.

4. COMPOUNDS INTERFERING WITH THE TEST

The usefulness of any qualitative test is, of course, largely determined by the number of compounds which will give the reaction in question. Masson [20] states that of all the substances dealt with in ordinary circumstances, water is the only one which has any chemical action on carbide. A consideration of the reaction between water and calcium carbide and that occurring in neutralization shows that in the presence of an acid water might be expected to form as rapidly as it is removed until the hydrogen of the acid has been quantitatively converted into acetylene by the following cycle of reactions:

$$\mathrm{CaC_2} + 2\mathrm{H_2O} = \mathrm{Ca(OH)_2} + \mathrm{C_2H_2}$$
$$\mathrm{Ca(OH)_2} + 2\mathrm{H(A)} = \mathrm{Ca(A)_2} + 2\mathrm{H_2O}$$

In the case of the weaker organic acids, at least, this does not take place, probably because of the fact that no neutralization occurs in a nearly anhydrous solution, and the formation of acetylene seems to give a good qualitative test for water in spite of the possible reaction between the acid and calcium hydroxide.

---

[20] Chem. News, 103, pp. 37–38 (1911); J. Chem. Soc., 97, p. 851; 1910.

Masson found that crystalline acids and acid salts, including those which contain water of crystallization readily removed by calcium carbide, do not react as acids, when treated with calcium carbide, with either the carbide or the calcium hydroxide resulting from reaction with the water of crystallization. Experiments by the author with acids in anhydrous solution showed that in some cases, at least, the acid in solution is quite as inactive as were the acids in Masson's experiments. Thus a 1 g sample of fused benzoic acid was dissolved in ether and boiled with calcium carbide under a reflux condenser for 15 minutes without producing a trace of acetylene. Solutions of oleic and phthalic acids have been found to behave in the same manner. Ordinary glacial acetic acid reacts vigorously with the production of acetylene, but neither acetic anhydride, nor acetic acid containing a considerable excess of acetic anhydride, do so. Sulphuric acid of all concentrations, including that containing an excess of sulphur trioxide, causes a continuous slow evolution of acetylene. Even in cases when acetylene is evolved on testing the weaker organic acids, it would, of course, be impossible to say, without first testing acids of known water content, how much, if any, of the acetylene was formed by the acid itself.

In his experiments upon the determination of water by the measurement of the acetylene evolved, McNeil[21] found that a larger volume of gas was evolved from glycerol and from oleic acid than could be accounted for by the amount of water present. In view of the behavior of related compounds, it seemed improbable that this could be due to the production of acetylene from the compounds themselves, except that in the case of oleic acid continuous neutralization and reaction with the water so formed might be expected to take place as with any other acid. In order to test this point, thoroughly dried samples of the two compounds were prepared. The large water content of the best samples available was not materially reduced by heating for three hours at 100°, in a stream of air dried over phosphorus pentoxide and at a pressure of less than half an atmosphere. The oleic acid was therefore dissolved in anhydrous ether, the ether distilled off under reduced pressure, and the acid heated to 110°. This operation was repeated several times. Glycerol was treated in the same way, using alcohol as a solvent instead of ether. By this procedure, both oleic acid and glycerol were obtained which did not give any trace of acetylene after contact with calcium carbide, either when used alone or in solution in ether or alcohol. An elevated temperature (as high as 120°) did not cause any reaction which could be detected.

---

[21] Bureau of Chemistry, Circular No. 97; 1912.

5. SENSITIVENESS OF TEST

This method for the detection of water is very sensitive. Numerous tests were made by the simple method of decantation of the solvent after contact with carbide, using samples of gasoline, benzene, and ether, which gave perfect blank tests. Known amounts of water were introduced by adding nearly absolute alcohol, the water content of which had been determined by E. C. McKelvy, of this Bureau, by the method of critical solution temperature.[22]

The results indicated about the same degree of sensibility in the case of the three above-named solvents, 0.01 to 0.03 mg of water per cubic centimeter of the solution in contact with the carbide being the limit at which the formation of a precipitate could be detected. Other tests made by adding a known weight of water dissolved in anhydrous ether showed about the same sensibility. Tests made upon other solvents, in which a blank test showed a trace of water, indicated that the test made with alcohol was less sensitive than with the solvents mentioned above, but more sensitive than with acetone. Ethyl acetate, chloroform and carbon tetrachloride showed about the same sensibility as ether.

SUMMARY

A colorimetric method for the detection of small amounts of acetylene has been developed in the course of an investigation upon the determination of small amounts of water by the use of calcium carbide. The results upon the quantitative determination of water have not been satisfactory, but a simple and very sensitive qualitative test for water is easily made.

The method for the determination of acetylene has been worked out successfully. The determination is made by conducting the gas to be investigated into an ammoniacal solution of cuprous chloride containing gelatine and alcohol, and comparing the red colloidal solution so obtained with a suitable standard, which may be either a solution of red dye or a piece of ruby glass.

---

[22] This Bulletin, 9, p. 344.

After a careful investigation of the effect of varying the composition of the absorbing solution the following procedure was adopted in making up the solution: Dissolve 0.25 g of gelatin in hot water, dilute to 500 cc, and add 500 cc of 95 per cent alcohol and 1.25 g of hydroxylamine hydrochloride. To 20 cc of this solution add 10 cc of concentrated ammonium hydroxide and a small amount of cuprous chloride. After the absorption of the acetylene the solution is diluted to 100 cc and compared in a colorimeter with the standard which has been chosen. The standard used in the experimental work was a solution containing chromanilbraun R, carmoisine B, and gum arabic. A more convenient, though less accurate, standard is a fixed depth of a solution of azolitmin. If 10 cm of a solution of azolitmin containing 1 part of the dye to 2500 parts of water is used as standard, the amount of acetylene in 100 cc of colloidal solution may be calculated from the equation $X = 0.13y + 0.03$, where X = number of milligrams of acetylene and $y = 10 \div$ number of centimeters of colloidal solution required to match the standard.

The method is very sensitive. Amounts of acetylene as small as 0.03 mg may be detected and amounts up to 2 mg may be determined with an accuracy of better than 0.05 mg.

Hydrogen sulphide and large amounts of oxygen and carbon dioxide interfere with the test, but all of these may be removed by passing the gas to be tested through a hot alkaline solution of pyrogallol without loss of acetylene.

A qualitative test for water, sensitive to less than 0.1 mg, may be very easily and quickly made by bringing the substance to be tested into contact with calcium carbide in the presence of a solvent for acetylene, which is then decanted or distilled into an ammoniacal solution of cuprous chloride. Nearly all the common organic liquids are suitable for use if carefully dried. The method is applicable to a great variety of substances and especially to volatile organic compounds. The only compounds known to interfere with the test are the stronger acids and substances, such as hydrogen sulphide, which precipitate cuprous salts from solution.

The investigation required some experiments upon the determination of larger amounts of acetylene by precipitation with cuprous chloride and subsequent determination of the copper. It was found that in order to obtain accurate results by this method it is absolutely necessary to carry out the filtration and washing of the precipitate in the absence of air.

WASHINGTON, November 2, 1915.

CONSTANTS OF THE QUARTZ-WEDGE SACCHARIMETER AND THE SPECIFIC ROTATION OF SUCROSE

I. THE CONSTANTS FOR THE 26-GRAM NORMAL WEIGHT

By Frederick Bates and Richard F. Jackson

CONTENTS

Page.

I. Introduction 68
- 1. Preliminary 68
- 2. The Ventzke scale 70
- 3. Scale of the International Sugar Commission 70
- 4. The Herzfeld-Schönrock investigation 71
- 5. Purpose and outline of the present investigation 73

II. Preparation of materials 75
- 1. Accessory materials 75
  - (a) Water 75
  - (b) Ethyl alcohol 75
  - (c) Methyl alcohol 75
- 2. Crystallization of sucrose from aqueous solution 75
- 3. Determination of ash 79
- 4. Elimination of reducing substances 79
- 5. Study of caramel formation 84
- 6. Elimination of moisture 87
- 7. Purification by precipitation with alcohol 92
- 8. Fractional crystallization 93
- 9. Preliminary polarization of purified samples 95
- 10. Description and designation of samples used in final series 96

III. Apparatus and manipulation 97
- 1. Volumetric flasks 97
- 2. Determination of the concentration of solutions 98
- 3. Preparation for polarization 99
- 4. Weights and thermometers 100
- 5. Polariscopes and thermostats 100
  - (a) The polarimeter 100
  - (b) The large thermostat 101
  - (c) The saccharimeters 101
- 6. Light sources 104
- 7. Quartz control plates 104
- 8. Polariscope tubes 105
- 9. Rotation produced by polariscope tubes filled with water 107

Page.
IV. Observations and computations.. 108
    1. Saccharimeter values of quartz control plates.................... 108
    2. $\frac{\phi^{20}\ \lambda=5892.5Å}{\phi^{20}\ \lambda=5461Å}$ for the normal sucrose solution...................... 109
    3. Corrections for temperature...................................... 111
    4. Determination of the reading of the normal solution on the Herzfeld-Schönrock scale.. 112
    5. The absolute rotation of the normal solution for the mercury line, $\lambda=5461Å$.. 116
    6. The absolute rotation of the normal solution for the sodium lines, $\lambda=5892.5Å$.. 118
    7. Determination of the conversion factor........................... 118
    8. Difference in circular degrees between the normal quartz plate and the normal solution.. 122
    9. Calculated difference in sugar degrees, for the normal solution, between white light with bichromate filter and $\lambda=5892.5Å$...... 122
    10. Rotation difference, in sugar degrees, for the normal solution, between $\lambda=5461Å$ and $\lambda=5892.5Å$...................... 123
    11. Thickness of the normal quartz plate............................. 124
    12. The specific rotation of sucrose.................................. 125
V. Summary... 127

I. INTRODUCTION

1. PRELIMINARY

One of the most important factors in the development of the sugar industry in the last few years has been the increased accuracy in the testing of sugars and sugar products. The same period has also seen an augmented use of the saccharimeter[1] as an instrument of precision for general scientific research. It is therefore important that all questions regarding the accuracy of the fundamental constants of sugar polarimetry[1] as well as any uncertainty regarding the basis of standardization be eliminated.

In the development of apparatus for the analysis of sugars the necessity for rapidity and simplicity has resulted in these factors being given consideration almost commensurate with that of accuracy. Thus, sugar-testing polariscopes are so designed that the reading of the scale gives the percentage of sucrose directly. This has been attained in the following way:

---

[1] Sugar in common with a large class of other substances alters or "rotates" the plane of vibration of plane-polarized light by an amount almost exactly proportional to its concentration. This property has been utilized for the exact analysis of these substances in instruments called saccharimeters and polarimeters.

Let the rotation, for plane-polarized light, of a 100 cc solution containing M grams of sucrose be ϕ. If a second solution contain M grams of an impure sugar in 100 cc, its rotation will be ϕ'. Let p be the per cent of sucrose in the impure sugar. Since the concentration of the first solution is M, the concentration of the second solution is $\frac{p\,M}{100}$. If we assume that the rotation of a sugar solution is proportional to its concentration, we have $p=\frac{100\,\phi'}{\phi}$. Hence, if ϕ be assumed 100 and the scale on which the rotation is measured be so marked when the first solution is read, the reading of the second solution gives directly the percentage of sugar present. Usage has designated M as the normal weight and the first solution as the normal solution. If M be a fixed value, ϕ is the rotation of the normal solution, and since it fixes the 100° S (see p. 71) point of the saccharimeter, its value in circular degrees for monochromatic light is a fundamental constant.

In practice it has long been found advantageous to control the reading of the scale by the use of the unchanging quartz plate, thereby obviating the difficult measurement with the normal sugar solution. The normal quartz plate may be defined as that plate which has the same rotation on the saccharimeter as the normal solution. It must read 100 on the quartz-wedge scale. In determining the value of a plate, however, it is desirable to take advantage of the high precision afforded by the polarimeter in which monochromatic light is used. It thus becomes necessary to know accurately the rotation in circular degrees of the normal quartz plate for the wave length of the monochromatic light source. This value is known as the *conversion factor*, because the value of any plate in terms of the normal sugar solution may be obtained directly by dividing its rotation in circular degrees by the $\frac{\textit{conversion factor}}{100}$. The value, once it is established, becomes the permanent record of the series of measurements which establish the 100° point of the saccharimeter. The accurate determination of the conversion factor is thus of great importance; and the necessity, for scientific and industrial purposes, that there be agreement on the magnitude of this constant by the different governments is apparent.

2. THE VENTZKE SCALE

Uncertainty regarding the exact basis of standardization has existed from the beginning of the development of methods for sugar testing. Ventzke[2] early proposed as the normal sugar solution one which should have at 17°5 a specific gravity of 1.100 referred to water at 17°5. This solution contains in 100 cc 26.048 g of sugar, weighed in air with brass weights. Subsequently the Mohr flask (100 Mohr = 100.234 cc) displaced the 100-cc flask and saccharimeter scales were graduated accordingly. Most of the instruments now in use are thus graduated according to the following definitions: The normal sugar solution[3] contains 26.048 g of sucrose, weighed in air with brass weights, in 100 Mohr cc at 17°5 C. This is polarized at 17°5 C in a 20-cm tube, the quartz wedges of the saccharimeter being at 17°5 C. Schönrock[4] determined the conversion factor for $\lambda = 5892.5$ Å[5] and obtained the value

$$
\begin{aligned}
&100^{\circ}\mathrm{V} = 34^{\circ}\!.68 \pm 0^{\circ}\!.02 \text{ at } 17^{\circ}\!.5 \text{ C or}\\
&100^{\circ}\mathrm{V} = 34^{\circ}\!.69 \text{ at } 20^{\circ} \text{ C.}
\end{aligned}
\tag{1}
$$

This measurement has never been made at the Bureau of Standards.

3. SCALE OF THE INTERNATIONAL SUGAR COMMISSION

Because of the confusion resulting from the use of the Mohr flask, and the inconvenience of a temperature of 17°5 C, the International Sugar Commission in 1900[6] adopted the following rational basis of standardization which has been generally applied by makers of saccharimeters:

(1) In general, all sugar tests shall be made at 20° C.

(2) The graduation of the saccharimeter shall be made at 20° C. Twenty-six grams of pure sugar, dissolved in water, and the volume made up to 100 metric cubic centimeters, or during the period of transition 26.048 g of pure sugar in 100 Mohr cubic centimeters, all weighings to be made in air with brass weights,

---

[2] Ventzke, Prakt. Chem., **25**, p. 84 (1842); **28**, p. 111 (1843).

[3] Landolt, Optische Drehungs-vermögen, p. 335 (1898).

[4] Schönrock, Zs. Instrk., **16**, p. 242 (1896).

[5] The Ängstrom unit (Å) which is commonly used in designating the wave-length of light is one ten-thousandth of a millimeter (10^{-4} mm).

[6] Zs. Ver. Zuckerind., **50**, I, p. 357 (1900); Wiechmann's Sugar Analysis, 3d ed., p. 222 (1914).

the completion of the volume and the polarization to be made at 20° C on an instrument graduated at 20° C, should give an indication of 100 on the scale of the saccharimeter.

(3) Preparation of pure sugar: Purest commercial sugar is to be further purified in the following manner: A hot saturated aqueous solution is prepared and the sugar precipitated with absolute ethyl alcohol; the sugar is carefully spun in a small centrifugal machine and washed in the latter with absolute alcohol. The sugar thus obtained is redissolved in water, the saturated solution again precipitated with alcohol and washed as above. The product of the second crop of crystals is dried between blotting paper and preserved in glass vessels for use. The moisture still contained in the sugar is determined and taken into account when weighing the sugar which is to be used.

The method of the international commission was early adopted by this Bureau as the official method. Saccharimeters designed for 26.048 g in 100 Mohr cc at 17°.5 C merely need to be controlled by a quartz plate standardized for 26 g in 100 cc at 20° in order that they may give polarizations nearly identical with saccharimeters designed for the new scale.

4. THE HERZFELD-SCHÖNROCK INVESTIGATION

The change in the basis of standardization made necessary a revision of the 100° point and a new determination of the conversion factor to replace the old value, 100° Ventzke[7] = 34°.69 circular degrees at 20° C. The investigations were made by Herzfeld[8] and his coworkers, in the Institut für Zucker-Industrie, and Schönrock[9] of the Physikalisch-Technische Reichsanstalt.

Ten quartz plates having rotations approximately equal to the normal plate were examined at the Reichsanstalt for optical purity, plane parallelism, and axis error. The rotation values in circular degrees for spectrally purified sodium light ($\lambda = 5892.5$ Å) were also determined at the Reichsanstalt. The rotation values in sugar degrees were measured at the Institut für Zucker-Industrie in conformity with the definition of the new sugar scale. The source of light was a Welsbach gas mantle. The radiation was filtered through a layer of a 6 per cent potassium bichromate solution 15 mm thick before it entered the polarizing system. The results of the investigation are summarized by Schönrock[10] in Table 1, where v is rotation in sugar degrees, α, rotation in circular degrees, and u, rotation of the normal plate in circular degrees: $u = \frac{100\alpha}{v}$ and $v' = \frac{100\alpha}{34.657}$

---

[7] Inasmuch as the word Ventzke in the expression 100° Ventzke or 100° V has become indissolubly linked with the older scale and thus conveys a definite idea of the values pertaining to that scale, its use has been confined to that scale at this Bureau. For the scale adopted by the international commission the word "sugar" has been adopted in order to avoid confusion; the term "100° sugar" or "100° S" corresponding for the new scale to the older term "100° Ventzke" or "100° V." It is hoped that this usage will become general. When not otherwise designated the circular degree is meant.

[8] Zs. Ver. Zuckerind., 50, II, p. 826 (1900).

[9] Zs. Ver. Zuckerind., 54, II, p. 521 (1904).

TABLE 1

Summary of Herzfeld-Schönrock Measurements

Plate No.	v in sugar degrees	α^{20} in circular degrees	u^{20} in circular degrees	v' in sugar degrees	$v-v'$ in sugar degrees
1	2	3	4	5	6
1 99	99.72	34.529	34.626	99.63	+0.09
2 99	96.97	33.577	34.626	96.88	+0.09
3 99	98.43	34.114	34.658	98.43	0.00
4 99	96.85	33.575	34.667	96.88	−0.03
5 99	100.97	35.035	34.698	101.09	−0.12
6 99	100.00	34.683	34.683	100.08	−0.08
7 99	99.99	34.640	34.643	99.95	+0.04
8 99	100.00	34.654	34.654	99.99	+0.01
9 99	99.97	34.638	34.648	99.95	+0.02
10 99	100.05	34.680	34.663	100.07	−0.02

Mean 34.657 E (10) = ±0.023.

The data show that

$$100^\circ \text{ sugar} = 34^\circ.657 \pm 0^\circ.023 \ (\lambda = 5892.5 \text{ Å}) \text{ at } 20^\circ \text{C.} \qquad (2)$$

which by definition is the rotation of the normal quartz plate. It will, however, be observed that the variations in the values of u are considerably larger than should be expected, the maximum deviation from the mean being 0°.041. Only a small part of each of these differences is to be sought in the values of α, and we are forced to conclude that considerable errors probably exist in the values of v. In fact, Schönrock[11] states that errors of 0°.10 S are possible.

---

[10] Loc. cit., p. 523.

[11] Loc. cit., p. 524.

5. PURPOSE AND OUTLINE OF THE PRESENT INVESTIGATION

For some years it has been noted at this Bureau that the normal sugar solution, prepared from samples, both of cane and of beet origin, issued by the Institut für Zucker-Industrie, reads less than 100° S on the saccharimeter scale. Because of this fact and of the necessity of the Bureau making careful scrutiny of the values of fundamental constants used in its standardizations, the following investigation was undertaken. Owing to the absence of a more accurate value, and the desirability of a uniform procedure among the different standardizing institutions, 34°.657 has thus far been accepted by the Bureau as the value of the conversion factor.

The value of the conversion factor determined by Herzfeld and Schönrock, as stated above, is for spectrally purified sodium light, the optical center of gravity of D_1 and D_2 being taken as 5892.5 Å. It is to be regretted that they did not measure the rotation of the normal solution in circular degrees. It has been shown[12] by one of us that the so-called yellow-green line, $\lambda = 5461$ Å of the mercury spectrum possesses marked advantages over $\lambda = 5892.5$ Å as the standard light source for polarimetric work. It is more stable, has a greater intensity, and is far easier to obtain pure at the high intensity required We have therefore utilized this mercury line as the fundamental source upon which all our measurements are either directly or indirectly based. With this source it is far easier to measure with high precision the rotation of quartz plates and of the difficultly prepared normal solutions. A smaller number of determinations is required and the labor of maintaining constant temperatures, preparation of materials, etc., is reduced. It is then possible to utilize accurately determined ratios to obtain the rotations for other light sources. Thus we have determined the conversion factor for $\lambda = 5461$ Å, and since the ratio, $\frac{\phi_{\lambda=5892.5\text{ Å}}}{\phi_{\lambda=5461.\text{ Å}}}$, where ϕ is the rotation of quartz, has been accurately measured at this Bureau, we may obtain the value of the conversion factor in terms of $\lambda = 5892.5$ Å, as well as calculate it by using the sodium values of the quartz plates. We have likewise determined a similar ratio for sucrose and thus obtained the rotation of the normal solution for $\lambda = 5892.5$ Å.

---

[12] Bates, Bull. Bur. Standards **2**, p. 239, Reprint No. 34 (1906).

A survey of the literature shows the large amount of work that has been done by different investigators upon the specific rotation, as compared with the other optical constants of sucrose, and the agreement between the different values found is such that we can assume the specific rotation to be known with considerable accuracy. Having determined the rotation of the normal solution for $\lambda = 5892.5$Å we have calculated the specific rotation and thus obtained a direct comparison of our work on the 100° S point with previous investigations on the specific rotation. We have also made many other experiments and with the aid of the data secured we have been able to secure values for a number of other important constants.

In carrying out this work we have devoted much effort to securing sucrose of as high a degree of purity as possible. Previous methods for the preparation of chemically pure sucrose have consisted almost exclusively of some mode of precipitation from aqueous solution by alcohol. While these methods, if great care in manipulation is taken and if the substance is not permitted to remain long in hot solution, are capable of yielding material of high purity, it seemed advisable in undertaking a study of the purification to utilize as great a variety of methods of preparation as possible.

The method of purification which has been of such importance in industrial sugar work, but which has been practically overlooked as a means of preparing the chemically pure substance, is that of crystallization from pure aqueous solution. As this method has proved a most economical one, both in respect to time and material, we have used it as our main reliance in preparing sucrose for the manifold uses of the Bureau of Standards.

II. PREPARATION OF MATERIALS

1. ACCESSORY MATERIALS

(*a*) WATER.—For the preliminary operations of purification once-distilled water was used; for the more careful work the water was redistilled after the addition of a small quantity of alkali and potassium permanganate. The first third of the distillate was rejected.

(*b*) ETHYL ALCOHOL.—Commercial grain alcohol was redistilled after the addition of caustic alkali. The first and final fourths of the distillate were rejected. For the more careful work the selected portion was redistilled and the middle fraction again selected. No attempt was made to eliminate moisture. The product answered the requirements of the present work if it was free from acids and if it evaporated without residue. The aldehyde content was too small to be made evident by the caustic alkali or silver nitrate tests.

(*c*) METHYL ALCOHOL.—The impure material was shaken with lime and distilled. The first and last fifths of the distillate were rejected. The middle portion was again distilled from lime and only the middle third utilized for experiment.

2. CRYSTALLIZATION OF SUCROSE FROM AQUEOUS SOLUTION

Through the courtesy of Dr. F. G. Wiechmann a quantity of the purest cane sugar of commerce was obtained. It was dissolved in distilled water to form a 40–50 per cent solution. This solution in addition to solid insoluble impurities contained suspended albumenoid material which had escaped clarification in the refining process. This material in the main passed through filter paper and was not entirely removed even after recrystallization. To remove it the dilute sugar solution was shaken thoroughly with a quantity of "alumina cream" which had been washed free from dissolved substances. It was then poured on large folded filters of hardened filter paper. The filtrate was brilliant in appearance and entirely free from suspended material.

The boiling of the solution to the required supersaturation was accomplished in the vacuum boiling apparatus, which is shown diagrammatically in Fig. 1. The entire assembly, with the exception of the aluminum vessel *B* and condensing coils *C*, is of glass, and with the exception of the small asbestos filter the sirup never comes in contact with any other substance. The evacuating is done by a pump connected at *D*. The solution is placed in the flask *A*, and the entire system evacuated up to the cock *E*. This cock is then carefully opened and the solution slowly driven through the asbestos filter into the boiling flask *F*, capacity 13 liters. Here it is warmed by the water bath, and the temperature of the sirup noted on the thermometer *G*. In order to obtain any desired boiling point it is only necessary to regulate the pressure. The degree of the vacuum is indicated by the mercury gauges *H H*. The efficiency of the assembly is such that sirup is rapidly brought to the desired concentration of about 80 per cent at a temperature below 32° C. This is made possible by the high efficiency of the condensing system and by having all joints carefully ground to a fit. The stop cocks are

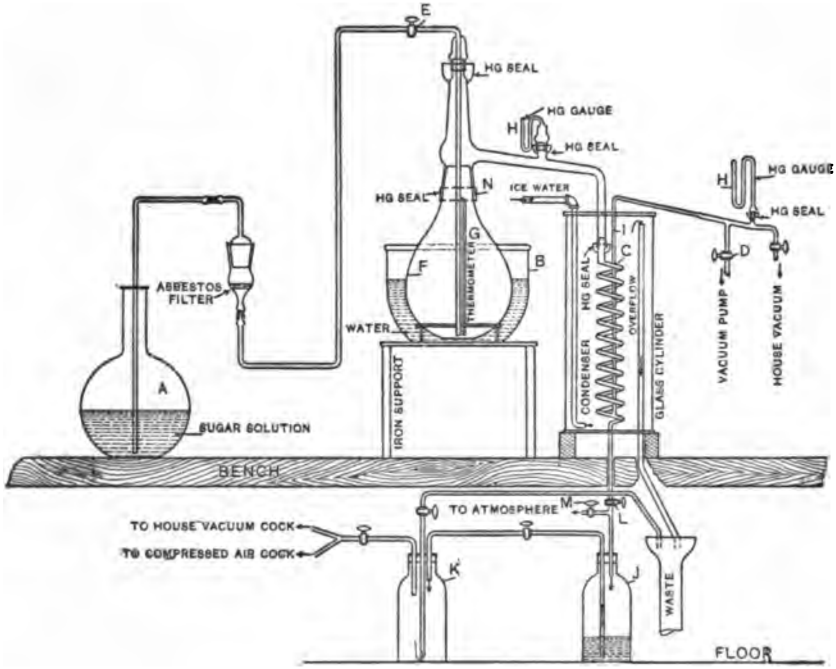


FIG. 1.—*Vacuum apparatus for concentrating sirups*

lubricated with water or sugar sirup. As rapidly as the vapors condense they pass into the vessel *J*, and subsequently by closing the cock *L* and opening *M* are expelled into *K*, from which the liquid is eventually driven into the waste.

The question of size of crystals is of the first importance. In general the smaller the crystals the less the included mother liquor. When the solution in the boiling flask *F* has reached the desired concentration, the vacuum is broken at *N* and the solution poured out to crystallize. Crystallization does not begin in these pure solutions until they are seeded with a few fine crystals of sugar. This is done after the solution is removed from the boiling flask. Two methods of crystallization were used. In the first the concentrated solution is transferred to a precipitation jar. It is then carefully stirred with a glass rod provided with a glass shield. This procedure gives satisfactory results so far as the size of crystals is concerned, but it is laborious. In the second the liquid is transferred to a crystallizer consisting of a glass flask or bottle held securely in a hardwood box mounted on bearings and driven by an electric motor. After standing overnight, the crystal mass is poured on a centrifuge and thoroughly drained of mother liquor.

After considerable experimenting with ordinary laboratory centrifuges, including the construction of three baskets in the Bureau of Standards shops, it was found that an especially designed centrifuge was necessary for the present work. A cross section of the one finally utilized is shown in Fig. 2. This centrifuge was built for this work by the International Instrument Co. of Cambridge, Mass., and has met all requirements. Its height over all is 2 feet, and it requires but 4 square feet of floor space. All surfaces with which either the crystals or the mother liquor can come in contact are silver or nickel plated. The basket is carried on the end of the vertical shaft of a three-fourths horsepower motor. It has an inside diameter of 9½ inches and is capable of carrying 10 pounds of sugar. The heavy cover is held in place by a number of set screws *A A* and may be readily detached in order to facilitate the removal of the centrifuged material. The lining to be satisfactory must retain very small crystals, permit of free drainage of the mother liquor, and be able to stand the severe strains incidental to high speeds. No single lining is available that will meet all these requirements. The built-up lining used consisted of two layers, the outer one being the regular copper centrifuge lining with elongated conical holes, and the inner of 200-mesh brass gauze. Both linings are silver plated. The small space between the lid and the frame is closed by stretching a rubber band tightly around the whole machine. When the centrifuge is in operation with the hinged lid *C* closed,

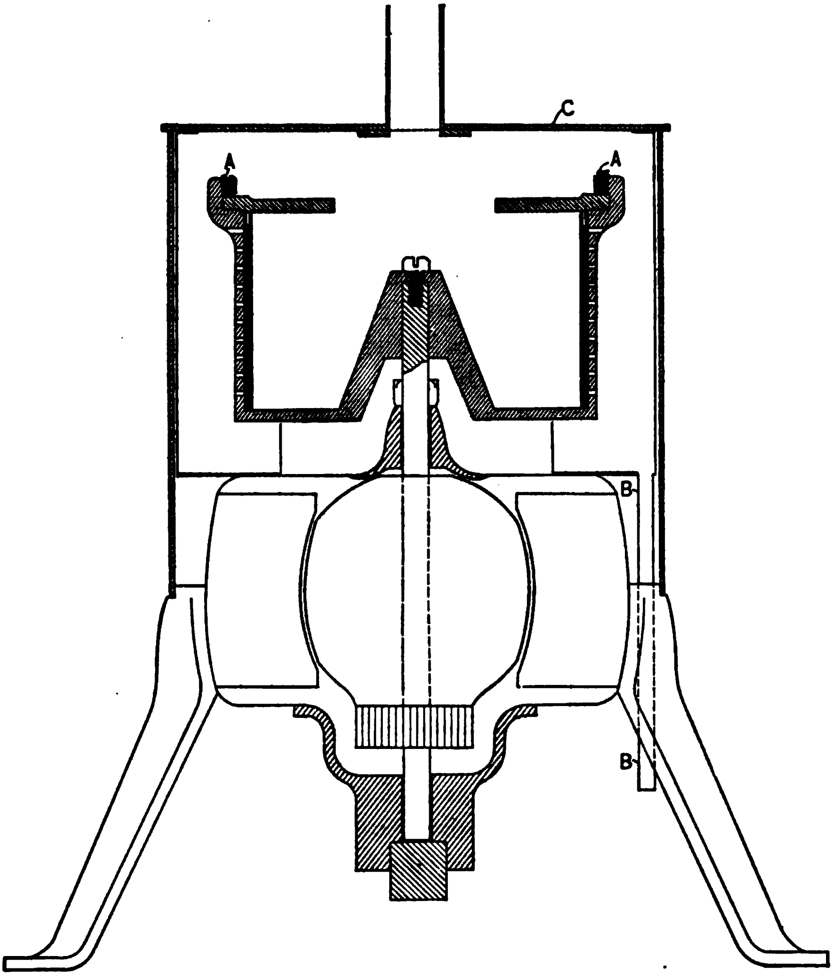


FIG. 2.—*Centrifuge*

the contents of the basket as well as the mother liquor are safe from contamination by the air of the room. The speed of rotation of the basket is controlled by a rheostat in series with the motor. In order to secure a proper distribution of the crystals and insure smooth running of the basket, the crystal mass is introduced while the machine is stationary or running at very low speed. The speed is gradually increased as the mother liquor runs off. Any desired number of revolutions per minute may be obtained up to 3000. After a thorough draining on the centrifuge the crystals are washed several times with pure redistilled alcohol, and finally placed to dry on a plate of glass carefully protected from dust.

With but little variation from this procedure a large number of samples were prepared and a study of the progress of the purification was made. What success in purification we attained, the following arguments are intended to show: If we assume that a given sample of sugar is contaminated by all sorts of impurities, these would be grouped in the following classes: (*a*) Soluble inorganic salts; (*b*) organic substances which reduce alkaline copper, such as invert sugar; (*c*) organic substances, possibly allied to sucrose, which do not reduce copper; and (*d*) moisture.

3. DETERMINATION OF ASH

Inorganic impurities are made evident by a determination of the ash. Inasmuch as most samples, after two recrystallizations, showed less than 0.1 mg of ash remaining from a 5 g sample, it was concluded that inorganic impurities were satisfactorily removed by this method of recrystallization.

4. ELIMINATION OF REDUCING SUBSTANCES

In the estimation of the small quantity of reducing sugar remaining after recrystallization, it was found to be impossible to make use of any of the published empirical tables, since these are based upon an assumed purity of the sucrose used in computing the tables, whereas the degree of purity of the sucrose is the problem to be solved. A few experiments served to show that the standard methods, in which are employed the various modifications of Fehling's solution with its large quantity of free caustic alkali, gave but little clue to the amount of reducing substances present. As an example, an experiment with the Soxhlet solution, according to the method of Herzfeld, yielded for a 10 g sample of the sucrose approximately 37 mg of copper, while a "sensitivity" experiment, i. e., an experiment in which a definite known quantity of invert sugar was added to the 10 g sample of recrystallized sucrose, showed that under these conditions 0.01 per cent, or 1 mg, of invert sugar caused an increase of precipitation of 2.5 mg of copper. Therefore, in interpreting the former analysis, we concluded that there were reducing substances present to the extent of 0.01 per cent $\times \frac{37}{2.5}$, or 0.15 per cent, in terms of invert sugar. The explanation of the apparently unfavorable result is that under these conditions sucrose is itself a substance having a slight reducing action.

Much more suitable for the present investigation, because of their slighter destructive action upon sucrose, are the solutions in which no free caustic alkali is used, but in which the latter is replaced by alkaline carbonates. Such, for example, are the Ost solution and a large number of others.[13] The Ost solution caused a precipitate of 10 mg of Cu_2O. The solution proposed by Striegler[14] caused a precipitate of about 7 mg, while an added impurity of 1 mg of invert sugar caused an increased precipitation of 3.2 mg of Cu_2O. This latter solution, because of its relatively slight destructive action upon sucrose and its high sensibility toward invert sugar in minute quantities, was deemed suitable for studying the progress of the purification. It contains in a liter 150 g $KHCO_3$, 101.4 g K_2CO_3, and 6.928 g of $CuSO_4.5H_2O$. Although particularly advantageous for the purpose in hand, this solution is not generally serviceable on account of its lack of stability on long standing. For an analysis 50 cc of the copper solution was brought to boiling and ebullition continued for one minute, then a 10 g sample of the sugar in a 50 cc solution was added and boiled for five minutes. At the end of this period the reaction was stopped by the addition of 100 cc of cold, recently boiled, water. The precipitate was filtered and weighed as Cu_2O. The weighing as cuprous oxide is justifiable when dealing with pure products. With this solution and method we made a study of the efficiency of the recrystallization, at each point determining the comparative purity of the sample with respect to that of the previous crystallization. A supply of granulated sugar was dissolved, clarified, boiled, and recrystallized in the manner described. The original sample caused a precipitation of 20 mg of Cu_2O; the recrystallized sample precipitated but 9 mg. A second recrystallization reduced the copper precipitate to 6.8 mg, while a third recrystallization failed to produce any further decrease in the reducing sugar. This precipitate of 6.5 to 7.0 mg proved to be a minimum quantity, for no sample which we prepared, utilizing all the precautions suggested by accumulated experience, produced a further diminution in reducing power.

---

[13] v. Lippmann, Die Chemie der Zuckerarten, I, p. 606 (1904).

[14] Ibid.

A sample of these crystals which precipitated 6.8 mg was dissolved and boiled in the vacuum apparatus in the usual manner, and at the end of the boiling, before crystals had formed, an analysis was made. Since 6.9 mg of Cu_2O were obtained, it was ascertained that no increase of reducing sugar content occurred during the solution and boiling. After crystallization and centrifuging, the crystals caused 6.7 mg of Cu_2O to precipitate, and a sample of the mother liquor containing 10 g of sucrose gave exactly the same precipitate.

From these experiments the conclusion was reached that, with respect to reducing substances, further recrystallization after the second could effect no improvement. Either a constant quantity of reducing sugar was present, distributing itself in a constant ratio between crystals and mother liquor, or sucrose itself effected the slight reduction of copper.

To test the latter point, analyses were made with other alkaline copper solutions in which the concentration of hydroxyl ion was diminished. The most satisfactory results were obtained with a modification of the Soldaini[15] reagent. The solution used contained in a liter slightly less than 300 g of $KHCO_3$, to which was added 1 g of copper sulphate crystals. The time of boiling was shortened to two minutes. The sample of sugar was dissolved in a 50 cc flask, from which it was poured into the copper reagent and the flask rinsed with 10 cc of water. The precipitate was finely divided, but was easily collected on a closely packed asbestos mat, or better, on a Gooch-Munroe-Nebauer crucible. An average of 13 determinations showed that a highly purified sample of sucrose produced a precipitate of 1.1 mg of Cu_2O. An average of 8 determinations, in which 0.01 per cent, or 1 mg of invert sugar, had been added, showed that 0.01 per cent of invert sugar caused an excess of precipitation of 1.9 mg. Therefore, from these analyses, it was concluded that the purified substance contained reducing substance not in excess of $1.1/1.9 \times 0.01$ per cent, or 0.006 per cent.

---

[15] v. Lippmann, Die Chemie der Zuckerarten, I, p. 606 (1904).

It seemed possible that even the small quantity of cuprous oxide precipitated under these conditions might, at least in part, be due to the action of sucrose itself. Since 0.006 per cent of invert sugar would be an optical impurity of nearly 0.01 per cent, it was deemed expedient to investigate the reactions involved in the analysis for reducing substances. Acting on the theory that there are two distinct reactions involved, the one the action of invert sugar or similar substances on the alkaline copper solution, the other the action of sucrose itself on the copper solution, we sought to ascertain if the two reactions had different velocities. For this purpose, the analysis was conducted in the same manner as before, with the single exception that the time of boiling of the mixed sample and copper solution was varied by whole minute periods from two to six minutes. The second column in Table 2 represents the weight of precipitate obtained with the purest sample of sucrose. The third column represents that obtained with the sucrose plus 1 milligram of invert sugar. Each figure in the table represents the mean of several determinations.

TABLE 2

Showing velocities of reaction of copper solution with sucrose and invert sugar

Time of boiling, in minutes	Precipitate obtained with pure sucrose	Precipitate obtained, sucrose+0.01 per cent of invert sugar	Precipitate caused by invert sugar alone—difference of columns 3 and 2
	mg	mg	mg
2	1.1	3.4	2.3
3	2.0	3.9	1.9
4	2.6	4.8	2.2
5	2.9	5.1	2.2
6	3.7	5.9	2.2

Let it be observed that the action of sucrose is progressive and practically linear with the time. The fourth column, obtained by subtracting column 2 from column 3, represents the reaction of the invert sugar upon the copper solution and it is at once seen that a distinct difference exists between the reaction of invert sugar, which is precipitated completely before the expiration of two minutes boiling, and that of the sample in question, which shows a progressive reaction. We must therefore conclude that the 1.1 mg of Cu_2O is caused in great part by sucrose itself.

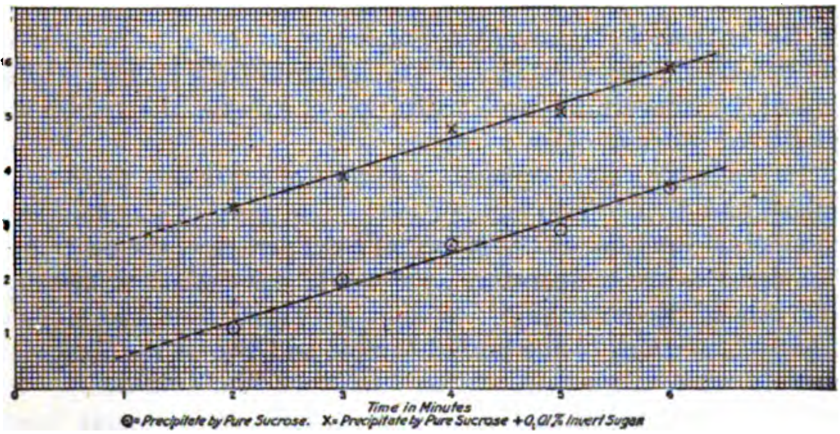


FIG. 3.—*Effect of duration of boiling upon weight of cuprous oxide*

If the velocity curves of the sucrose and of the sucrose invert sugar mixture be plotted as in Fig. 3, and both curves be produced to cut the axis at zero time, we find that the sucrose curve cuts it at approximately the origin, while the sucrose plus invert sugar curve intersects it at the point representing a weight of Cu_2O equivalent to the invert sugar added. This construction is permissible because the invert sugar reaction is complete before two minutes have elapsed and we may consider it for the purposes of this argument as instantaneous, or rather, we may say that these experimental results would be the same if it were instantaneous. If, therefore, any reducing substance other than sucrose itself is present, it is of the order of 0.001 per cent and entirely negligible.

5. STUDY OF CARAMEL FORMATION

The elimination of the last traces of moisture from the sugar necessitated a thorough knowledge of the effect of a high temperature on dry sucrose. It is well known that slightly above the melting point sugar passes rapidly into one of the varieties of caramel. Even far below the melting point the change occurs slowly and even at 100° C discoloration can be observed after several hours. By means of the reaction of caramel with the alkaline copper solution, minute changes could be observed quantitatively.

The analysis for caramel was conducted in the same manner as for other reducing substances. On account of the lack of precise knowledge concerning the constitution of caramel the results are expressed in terms of invert sugar.

In conducting an experiment a sample of sugar was thoroughly mixed and divided into two portions. One portion was kept in a stoppered container at the laboratory temperature, the other was subjected to the temperature at which it was desired to measure the rate of decomposition. When the desired time had elapsed two 10 g portions of the heated sample and two of the unheated sample were taken and all four analyzed simultaneously. At each temperature successive tests were made at increasing intervals of time in order to observe the course of the reaction. For the relatively small extent of the decomposition investigated, the velocity was approximately constant. The period of heating was continued until the decomposition was sufficient in amount to render the determination of velocity sufficiently accurate.

Table 3 gives in summary the results of these experiments. At each temperature is given the length of time necessary to effect a decomposition equivalent to 0.01 per cent of invert sugar. This decomposition depends somewhat upon the size of the crystals and these data apply only to the very fine particles used in this investigation.

TABLE 3

Length of Time at each Temperature Required to form Caramel Equivalent to 0.01 Per Cent Invert Sugar

Temperature, °C	100°	79.5	66.6	50.0	39.0
Time in hours required to form caramel equivalent to 0.01 per cent invert sugar	0.015	0.57	10.9	107.0	476

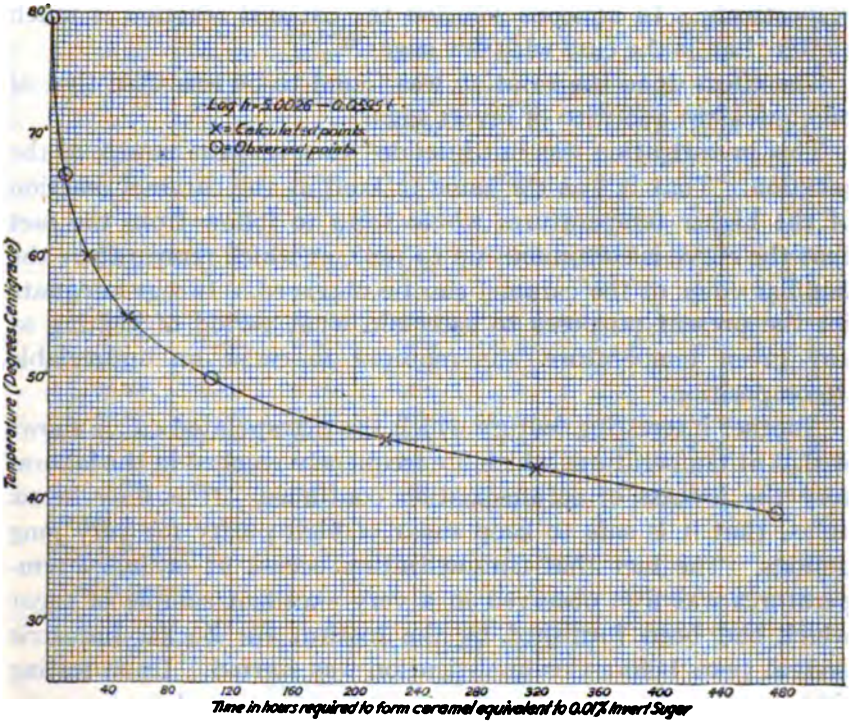


FIG. 4.—*Velocities of caramel formation at various temperatures*

It may be seen that the caramelization reaction occurs at much lower temperatures than is commonly supposed and it is unquestionably one of the factors in the determination of moisture in saccharine products. The data in Table 3 are shown graphically in Fig. 4.

This decomposition varies considerably with altered conditions. The same crystals at the same temperature but in a vacuum decompose at a much lower velocity. Furthermore, an increase in the size of the crystals exercises a considerable influence upon the reaction. Three samples, consisting of the finely pulverized crystals of our own preparation, a quantity of ordinary granulated sugar, and a number of crystals of Kahlbaum's rock candy, were heated until some decomposition had occurred. The powdered sample increased its reducing power by 5.4 mg of copper, the granulated sugar, and the rock candy by 1.2 mg and 1.3 mg, respectively. In aqueous solution the caramel reaction is much slower than is the case with dry sugar.[16]

The effect upon the rotation was found to be less than that of an equivalent quantity of invert sugar.

This investigation was not intended to reveal the nature of the reaction. That it was the same in kind as the caramel reaction of the higher temperatures would seem to follow from the fact that the curve is continuous up to 100°, at which temperature the familiar color of the caramel can be observed. It was adequate for the present purposes to ascertain what period of heating at any given temperature was required to cause an appreciable decomposition.

Another interesting feature which the extrapolated curve shows is that at temperatures which are frequently reached in the laboratory the process of caramelization continues. It is only below 20° C that it is safe to keep sugar of high purity for very long periods. The fact that caramelization occurs at ordinary temperatures was first observed in a very excellent sample of sugar which had been furnished by the Institut für Zucker-Industrie several years before this investigation was started. Upon testing this sample for reducing substances, it was found to be quite inferior, but the high reducing power was later recognized to be due to caramel formation. The low polarization of this material also indicated the presence of impurity. (See experiment No. 17, Table 4.) This same phenomenon has been observed in many of our own purest samples of sucrose. For our own purposes, then, it was necessary to have comparatively fresh samples of sugar.

---

[16] Aulard, Orig. Comm. VIII Int. Cong. Appl. Chem., 25, p. 493 (1912).

TABLE 4

Preliminary Series of Saccharimeter Measurements at 20° C on Approximately Normal Sugar Solutions on the Herzfeld-Schönrock Scale

Experiment number	Weight sugar (air, brass weights)	Weight solution (air, brass weights)	Sugar by weight in vacuo	Density, K.N.E.K. table	Volume of solution— Computed from weight and density	Volume of solution— By flask mark	Average rotation of solution on two saccharimeters	Rotation of normal solution
	g	g	Per cent		cc	cc	Degrees sugar	Degrees sugar
7	25.975	108.943	23.835	1.09822	99.293	99.284	100.48	99.86
8	25.673	108.823	23.584	1.09707	99.288	99.284	99.29	99.87
9	27.156	109.857	24.712	1.10223	99.761	99.757	104.57	99.89
10	25.840	109.928	23.499	1.09669			98.97	99.92
11	25.958	109.820	23.629	1.09728			99.58	99.92
12	23.978	101.429	23.633	1.09730	92.522	92.518	99.55	99.88
13	32.833	142.196	23.084	1.09480	129.996	130.001	97.06	99.92
14	26.073	109.804	23.737	1.09777			100.03	99.89
15	24.016	101.443	23.667	1.09745	92.522	92.518	99.67	99.86
16	24.000	99.127	24.204	1.09990			102.20	99.87
17	26.053	109.883	23.702	1.09770			99.79	[a] 99.78
18	25.999	109.925	23.644	1.09735			99.62	99.89
19	23.970	101.425	23.625	1.09726	92.521	92.518	99.51	99.86
20	34.251	143.003	23.966	1.09882	130.142	130.138	101.09	99.87
21	24.560	101.649	24.154	1.09967	92.522	92.521	101.92	99.83
22	23.987	101.431	23.642	1.09734	92.519	92.518	99.60	99.89
23	25.974	109.340	23.748	1.09782	99.691	99.687	100.04	99.83
24	26.588	110.108	24.139	1.09961			101.85	99.83
25	26.105	108.395	24.075	1.09931			101.60	99.87
Average								99.875
Mean scale correction								.024
Corrected average								99.90

[a] Not included in the average. (See p. 86.)

6. ELIMINATION OF MOISTURE

In order to prepare the sugar for the final weighing before polarization it was necessary to eliminate the final traces of moisture. The period of time at each temperature during which it was possible to heat the substance without causing decomposition was definitely established by the caramelization experiments. In these operations a wide margin of safety was adopted.

For a preliminary preparation and drying, the air-dried crystals were ground in an agate mortar, the pestle of which was equipped with a dust shield. In some cases the material was transferred to a crystallizing dish and placed in a vacuum desiccator over quicklime. In other instances it was introduced directly into the weighed volumetric flask and the total weight observed. Flask and sugar were then subjected to the final drying operations and the diminution of weight closely followed. It was evident from early experiments either that the residual moisture was present only in very small quantities or that it was held with great tenacity. To test this point a variety of experiments were performed, of which the following are typical:

(1) The flask containing the sample was placed in a large glass tube 70 mm in diameter fitted with a large, perfectly matched glass grinding which was lubricated with a rubber-vaseline stopcock grease. The drying agent was placed in a porcelain boat. The tube was then connected with a vacuum pump and McLeod gauge and the air exhausted until a residual pressure of 0.01 mm to 0.0001 mm of mercury was reached. The drying agent consisted usually of a quantity of calcium chloride or calcium oxide which had been recently ignited in an electric muffle furnace. Calcium oxide was used for drying all the samples used in the final series of measurements. Simultaneously with the pumping, the sample was heated uniformly by an electric oven to a temperature of 50° to 70° C. The latter temperature was never maintained for a period greater than two hours. The results of these experiments were invariably the same. The air-dried and pulverized sample lost in weight about 0.01 or 0.02 per cent at the first drying operation, provided the conditions favorable to elimination of moisture were sufficiently thorough. For this preliminary drying the sample was usually exposed to the drying agent for 24 hours or more at a pressure of 0.01 mm or less and a temperature of 50° C. Nevertheless, the rule followed in every case was to repeat the operation with more thorough procedure until a constant weight was obtained. This second operation was carried out at a higher temperature (with care to avoid caramel formation) or for an increased length of time or at higher vacuum. The air admitted to break the vacuum was passed through a drying train, consisting of H_2SO_4, P_2O_5, and CaO. The connection to the drying train was made by breaking the tip of the capillary

of the drying tube inside a short piece of clean rubber pressure tubing. The results of this second operation were uniformly the same. In no case was a loss of weight greater than one-half milligram or 0.002 per cent found, and in the great majority of instances identical weighings were obtained after the first and second drying operations.

This experiment was carried out repeatedly during the preliminary series of measurements. In two instances phosphorous pentoxide was used as a drying agent, but it produced no further desiccation than freshly ignited calcium oxide.

In order to be certain that the small diameter of the neck of the volumetric flask did not act as a deterrent to the passage of water vapor at the high vacuum, the same experiment was tried with the sugar contained in a shallow porcelain boat. The boat was pushed into a weighing bottle and stoppered before removing from the dry air of the tube. The results of this experiment were similar to the others.

(2) A sample which had been subjected to the usual preliminary drying in a porcelain boat was further treated by exposure to a stream of air dried by successively passing H_2SO_4, P_2O_5, and CaO. In the meantime it was subjected to a temperature of 70° for two hours, and 80° for one-half hour. A weighing bottle was also placed in the tube in such a way that the boat could be pushed into it and the stopper inserted while in contact with dry air. This experiment produced no further desiccation beyond the simple exposure to high vacuum and quicklime.

(3) A sample which had been introduced into a long, narrow volumetric flask and dried for 48 hours over lime was weighed and placed in a glass tube, together with freshly ignited quicklime. The tube was drawn down and sealed to the glass parts of the mercury pump. A portion of the connecting tubing dipped into carbonic acid snow during the evacuation. When a vacuum of 0.0001 mm was registered by the McLeod gauge the tube was sealed off. This was allowed to stand for a period of five months during an interruption of the work. Dry air was then admitted by breaking the tip of the capillary, while inside a piece of clean rubber tubing connected with the drying train. The

stopper was inserted while in the dry air by the action of a magnetic field on a small iron rod, which was sealed in a glass frame and which in turn held the stopper centered.

This long period of drying produced no further desiccation. The polarization of the sugar is recorded in experiment 25 of the final series.

(4) Finally a sample, which had been placed in a long, narrow flask and dried to a constant weight, was inserted in a glass tube, together with fresh quicklime, and the tube drawn down and sealed to the glass portions of a Gaede rotary mercury pump. A portion of the connecting tube dipped into liquid air to remove the mercury vapor. The sample of sugar was heated to 50° C, and was subjected to the highest vacuum which the Gaede pump would produce. This, as indicated on the McLeod gauge, was better than 0.0001 mm, and probably represented the absolute pressure, since mercury vapor was now absent from the tube containing the sugar. After some hours the tube was sealed off and allowed to remain over night. The sample suffered no loss of weight.

Water may be present in a sample, either as surface moisture existing as a film or as included mother liquor. In the first case the quantity would depend on the fineness of the crystals. It would be, moreover, the only moisture removed by the drying agent. The included moisture could hardly be expected to rupture the crystal and escape. The method of crystallization in motion and the fineness of the crystals would almost preclude the possibility of any considerable amount of included mother liquor. The following experiment corroborates this conclusion. A sample was selected in which for some reason the crystals had developed to considerable size—as large as a fine sample of granulated sugar. This was dried without pulverizing, and its polarization determined. Another portion of the same sample was then pulverized extremely fine, dried, and polarized. These two samples yielded nearly identical polarizations. (See experiments Nos. 20 and 22.) We concluded, therefore, that even when the crystals were large enough to be visible no considerable quantity of solution was included. Much less, then, is the probability when the crystals are extremely fine and are further reduced by grinding. This conclusion would be invalidated if the liberated mother liquor were exactly compensated by increased surface moisture. This latter possibility, in view of our various drying experiments, seems remote.

The accumulated evidence of all desiccation experiments led us to the conclusion that the very simple expedient of drying sugar by means of a vacuum of one-thousandth of a millimeter of Hg over freshly ignited quicklime leaves residual moisture in amount small enough to be negligible. To corroborate this conclusion it remained to apply direct tests for the presence of moisture. Two sensitive tests were applied.

E. C. McKelvy, of this Bureau, has used the critical solution temperature [17] of an alcohol-oil mixture as a criterion for the absence of moisture, and has shown that the same method is applicable to the detection of moisture in a third substance.[18] The presence of 1 per cent of water in alcohol causes a rise in the critical solution temperature of 16 whole degrees. Since a change of a few hundredths of a degree can be detected, the method offers a means of identifying a small quantity of water in a sample of alcohol. In order to test a third substance for moisture, it is necessary to digest it with a sample of dry alcohol, whose critical solution temperature with a given oil has been already determined in blank, and then to apply the test to the alcohol after the digestion. This test involves the assumption that any moisture on the third substance distributes itself between the dry alcohol and the substance. From the digestion flask the alcohol is distilled and subjected to the solution temperature test. Since ethyl-alcohol water mixtures show a minimum boiling point at 96 per cent by weight of alcohol,[19] the first portions of the distillate will be richer in water than the remaining portions if the amount of moisture in question is small. The latter should then take more moisture from the substance to keep the same distribution ratio. Consequently a great portion of the moisture should appear in the alcohol distillate. A comparison of the critical solution temperature of the distillate with the original alcohol should show at least qualitatively the presence of moisture. This experiment was very carefully carried out on a sample of dried sugar by Mr. McKelvy and practically negative results obtained. It is a pleasure to thank Mr. McKelvy for this work.

---

[17] Bull. Bur. Standards, 9, p. 328 (1913).

[18] Science, 38, p. 711 (1914).

[19] Noyes and Warfel, J. Am. Chem. Soc., 23, p. 467 (1901).

E. R. Weaver, of this Bureau, has described[30] a test for a minute quantity of moisture. This test consists of the generation of acetylene by a reaction of the moisture with calcium carbide. The acetylene is allowed to react with an ammoniacal solution of cuprous chloride to form copper carbide.

The sample of sugar dried in the usual way was placed in a glass apparatus consisting essentially of three parallel test tubes sealed in a triangle at their tops. A quantity of dry ether was poured on the sugar and after a few minutes digestion was distilled into the second test tube which contained calcium carbide. It was then distilled into the third tube whence it was poured directly into the cuprous chloride solution. The results were entirely negative. To another portion of sugar the dry ether was added and fragments of carbide were placed directly in contact with the sugar. After some shaking the ether was distilled and poured into the cuprous chloride solution. Again the results were negative. About 10 g of sugar were used in the latter experiment. The method is capable of detecting 0.1 mg of moisture. One milligram of water gives a very deep color. The quantity of moisture on the sugar must then have been of the order of one-thousandth of 1 per cent. We are glad to express our indebtedness to Mr. Weaver for this experiment.

7. PURIFICATION BY PRECIPITATION WITH ALCOHOL

The dilute solution was prepared in the manner described above. It was filtered and boiled in the vacuum apparatus until the desired concentration was reached. This concentration was usually about 70 per cent with occasional variations above and below depending upon the alcohol used for the precipitation. An equal volume of alcohol was added and the whole rotated in the crystallizer over night or until crystallization was complete. This procedure has the advantage of permitting very complete clarification and filtration while in dilute solution and of avoiding the hot saturated solution which is difficult to filter and dangerous to the sucrose.

---

[30] J. Am. Chem. Soc. **35**, p. 1310 (1913); **36**, p. 2462 (1914); Bull. Bur. Standards **13**, p. 27 (1916).

8. FRACTIONAL CRYSTALLIZATION

The method of purification by crystallization from aqueous solution permits the utilization of the mother liquor. In many instances this was simply boiled down in a vacuum and another lot of crystals obtained. The opportunity that this method affords for a fractional crystallization for the elimination of impurities of class *c* (see p. 79) is of great importance in the present investigation.

About 18 kg of granulated sugar (designated fraction 1) was recrystallized in the manner previously described. The new crystals (fraction 3) were recrystallized. The twice-crystallized portion was called fraction 6 and its mother liquor fraction 5. The first mother liquor (fraction 2) was reboiled and recrystallized. The crystals being the lesser soluble portion of the more soluble part of the original substance were presumably of similar composition to fraction 5, since the latter was the more soluble portion of the less soluble part of the original substance. These crystals were consequently combined with fraction 5 and the whole recrystallized. The new crystals formed a portion of fraction 9 and the new mother liquor became a portion of fraction 8. The fractionation is illustrated in Fig. 5. Each number represents a fraction. Those inside the diagram indicate a combination of the previously obtained crystals and mother liquor. The unnumbered ends of lines extending from the left of the figure indicate that the respective mother liquors were rejected. Impurities of lesser solubility than sucrose tend to concentrate at the right side of the diagram, those of greater solubility at the left side. Unfortunately, owing to interruptions in the work, several fractions were allowed to remain in solution for long periods of time and consequently suffered some inversion. When the work was resumed, the crystallization was continued until the invert sugar was in the extreme fraction. It was found necessary to reject several fractions which otherwise could have been utilized for test. Nevertheless, the careful measurements of fractions 30–b, 31–b, 32–a, 27, and 21 indicate that the impurities in the original sample appear only in the mother liquors. Among these impurities must have been any raffinose which may have been present. The fact that this substance is present to such an extent in beet molasses would make it seem probable that recrystallization from water would remove it. If it had still persisted in the crystals, it should have concentrated itself in some fraction after so many fractionations. The essential identity of the various fractions tested indicates the absence of this and similar substances from the recrystallized sucrose.

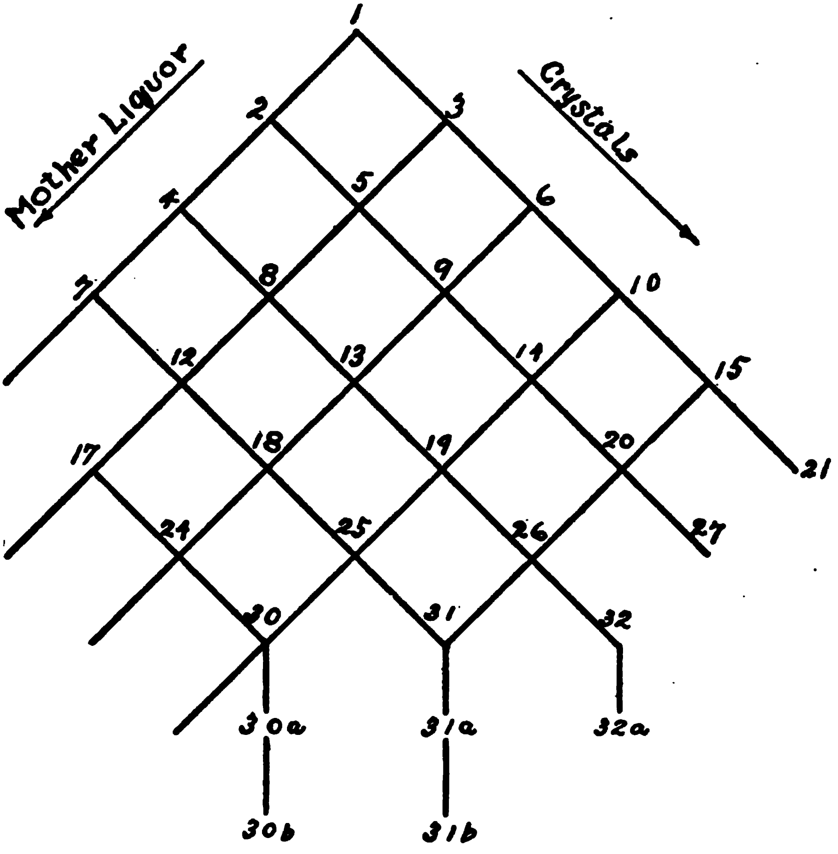


Fig. 5.—*Diagrammatic representation of fractional crystallization*

Fractions 30, 31, and 32 required one or two recrystallizations to remove small quantities of invert sugar.

9. PRELIMINARY POLARIZATION OF PURIFIED SAMPLES

The measurements recorded in the preliminary series, Table 4, were all made with samples of sugar which had undergone at least two recrystallizations. Experiments 7 to 13 were made with various samples prepared from the refined sugar of commerce. Many of the samples were obtained by recrystallization of the mother liquors. In experiments 14 and 15 the samples were precipitated by alcohol. In No. 16 the sugar was prepared from European raw-beet sugar which in the crude state polarized about 95° S. This was purged with water, clarified with alumina cream, and several times recrystallized. In experiment 17 the sugar supplied by the Institut für Zucker-Industrie was used. It has been shown on page 86 that this contained a considerable quantity of reducing substance and consequently its rotation was not included in calculating the average. Experiments 19 and 21 were made upon fraction No. 15 of the fractionally crystallized sugar described on page 93. Experiment 22 was a measurement of fraction No. 20. Experiments 20 and 22 were made upon fraction 21 and experiment 24 upon fraction 27. In experiment 35 the final purification of the sample consisted of a precipitation with purified methyl alcohol. This reagent was used because of its well-known solvent effect upon raffinose and because it offered a further variation of procedure. The result was not included in the final series because the polariscopic readings were taken by only one observer.

The preliminary measurements were continued until the procedure was entirely satisfactory. In each experiment the zero points and rotation values were observed and the averaged rotation corrected for concentration by the method described on page 115. The scale correction is obtained from Table 8. The Julius Peters instrument was not used in the preliminary series. It will be observed that the value 99°.90 S for the reading of the normal solution on the Herzfeld-Schönrock scale serves to corroborate the value obtained in the final series.

A paper describing the preliminary series of measurements in substantially the form here presented was read before the Eighth International Congress of Applied Chemistry[21] at New York in 1912. It resulted in the appointment of a subcommittee to report upon the advisability of adopting the new standard.

---

[21] Orig. Comm. Eighth Int. Cong. Appl. Chem. 25, p. 517 (1912).

10. DESCRIPTION AND DESIGNATION OF SAMPLES USED IN FINAL SERIES

It is of importance to ascertain whether the alcohol used could have a harmful effect upon the sucrose. Such an effect could conceivably occur by actual combination of alcohol with sucrose to form an unknown substance which could have a very different rotary power from sucrose. Although in the absence of a catalyzer this possibility was remote, yet it seemed advisable to investigate the question. In the method which has been our main reliance, alcohol was used only in the final washing of the crystals. In the method prescribed by the international committee on uniform sugar analysis the sugar is precipitated in hot solution by alcohol. Samples A and B were prepared by methods offering the greatest possible contrast as far as the use of alcohol is concerned. To prepare sample A a quantity of sugar collected from miscellaneous samples, which had been previously twice recrystallized was recrystallized from aqueous solution in the usual manner and washed with pure water while on the centrifuge. No alcohol was allowed to come in contact with the sugar during its final preparation. During the air-drying the substance was frequently stirred to prevent the formation of cakes. A test with the copper solution showed the absence of reducing substances.

For the preparation of sample B the mother liquor from sample A was warmed with more pure sugar to form a sirup of about 70 per cent concentration. To this sirup an equal volume of pure alcohol was added and the mixture kept at a temperature of 50° C to 70° C for about 48 hours. The whole was then allowed to cool and crystallize while in continuous motion. The crystals were centrifuged and washed with alcohol. It was desired by this experiment in contrast to sample A to exaggerate any effect that might be due to the presence of alcohol. A preliminary measurement, experiment 18, showed that the sample possessed the same rotary power as the other material, and it was consequently used in the final series.

Sample C was prepared by recrystallization of the unused portion of sample A. The new crystals were washed with alcohol.

The remaining samples used in the final series were taken from the fractionated sugar, the preparation of which was described on page 93.

III. APPARATUS AND MANIPULATION

1. THE VOLUMETRIC FLASKS

A number of volumetric flasks, Fig. 6, were made for the purposes of this investigation from Jena normal 16^{III} glass. In the construction of these flasks no attempt was made to adjust them to exactly 100 cc, but rather attention was paid to placing the graduation mark at the most advantageous position on the neck.

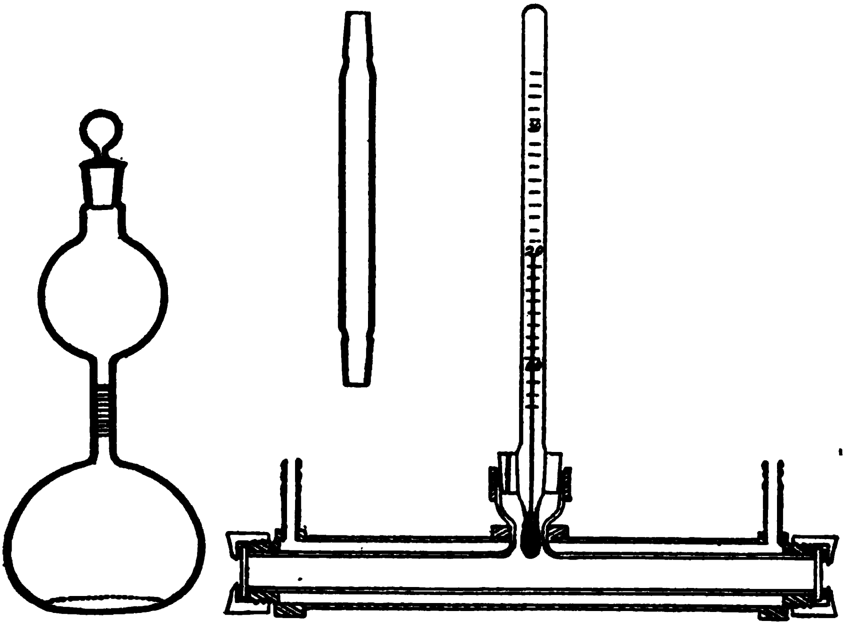


FIG. 6.—*Volumetric flask, polariscope tube, and glass connection used in conveying solution to tube*

The diameter of the neck at the graduated portion was from 5 to 7 mm. Above the graduation the neck was blown out into a bulb of about 30-cc content and at the upper end was fitted with a grinding. In two instances the necks were provided with a series of 10 graduations 0.02 cc apart. With suitable precautions the volume could be estimated to the tenth part of one of these divisions.

The flasks were calibrated by filling at 20°00 C with distilled water which was freed from dissolved air by boiling in a vacuum.

Before the final adjustment the neck of the flask above the meniscus was dried by a stream of filtered air. The temperature was adjusted by immersing the flasks in the water of a thermostat which remained constant within 0°.01. The conditions for adjusting the volume of the water in the volumetric flasks were so favorable that it was found possible to reproduce the weight of contained water to 0.002 g.

2. DETERMINATION OF THE CONCENTRATION OF SOLUTIONS

In the determination of the concentration of the solutions for polarization two methods were used, both of which in many instances were applied to the same solution in order to obtain corroborative values.

The first method consisted of weighing the sugar in the flask and making the solution up to the graduation mark after the temperature had been adjusted. If, as in the two above-mentioned instances, the flask possessed a series of graduation marks, instead of a single one, the volume of solution was carefully read off to the tenth of one division. In making up sugar solutions the same procedure was followed as for the calibration of the flasks.

The second method of determining the concentration consisted of computing the percentage concentration and calculating the volume by dividing the total weight of solution in vacuo by the density of solution, the latter being obtained by reference to the density tables of the Kaiserliche Normal-Eichungs-Kommission.[22]

These two methods of determining the volume of solution checked in every instance but two to 0.005 cc or better. When the two methods were used the mean of the two determinations was taken as the volume of the solution.

It was observed that the more favorable the conditions were for making the solutions to volume, the more closely the volumetric and gravimetric methods agreed. The conditions which were subject to variation were temperature and condition of the meniscus. This agreement led us to place increasing confidence in the density tables, and in many instances the solutions were made up by the gravimetric method alone.

---

[22] Plato, Wiss. Abh. der Kais. Normal-Eichungs-Kommission, **2**, p. 153 (1900). Circular Bur. Standards, **19**, p. 26 (1914)

In determining the correction for buoyancy of air for the preliminary series the value of the average density 0.0012 was assumed. For the final series the air density was determined from the temperature and barometer readings. The widest probable variations from 0.0012 would have affected the weight of the sugar or solution by a negligible quantity. For the density of dried pulverized sugar the value 1.59 was used. This is approximately the mean of the determinations of a large number of observers as well as the rounded-off figure given by Plato[23] and his coworkers.

3. PREPARATION FOR POLARIZATION

To perform a polarization a quantity of sugar, approximately 26 g, was transferred to a weighed flask and the flask again weighed after standing in the balance case. Sugar and flask were then subjected to the various drying operations previously described until assurance was had that a constant weight had been attained. Water was then added, the sugar dissolved, and the neck of the flask carefully washed down. The flask was nearly filled and the resulting solution boiled in a vacuum until the evolution of dissolved air ceased. Loss by spattering was carefully avoided. The flask and solution were then placed in the thermostat and, when a temperature of 20° had been attained, were adjusted to volume. Before weighing, the temperature of the solution was changed to approximately that of the balance case. The flask was wiped with a slightly damp cloth and allowed to remain an hour before its weight was recorded.

The solution was then carefully mixed by continually spilling into the portion of the neck enlarged for that purpose, and finally poured into the polariscope tubes. This process was carried out by means of a glass tube, Fig. 6, with grindings at both ends, one of which fitted the volumetric flasks and the other the grindings of the polariscope tubes. In this way the transfer to the tubes was accomplished without evaporation and consequent concentration of the solution. The grinding of the polariscope tube was then tightly stoppered with a glass stopper or with a thermometer.

---

[23] v. Lippmann, Die Chemie der Zuckerarten, II, p. 1067 (1904).

4. WEIGHTS AND THERMOMETERS

The weights used were tested by the division of weights and measures of this Bureau by comparison with the official standards. All weighings were made by the method of substitution, a flask of similar size and shape serving for a counterpoise.

The thermometers were tested by the division of thermometry of this Bureau.

5. POLARISCOPES AND THERMOSTATS

(*a*) THE POLARIMETER.—One instrument for absolute rotation and three saccharimeters were used. The former is a special polariscope built to order for the Bureau of Standards by Franz Schmidt & Haensch. It is capable of a wide range of adjustment. The massive base rests on a three-point support and is accurately machined to permit of varying the distance between the polarizing and analyzing systems. The nicol prisms are of superior quality. The large nicol of the Lippich half-shade polarizing system is of the Glan-Thompson type and has an available opening of 14 mm. The perfection of the prisms, combined with the large apertures, make possible a high degree of sensitivity even with a 200 mm tube of solution in the instrument. The circular silver scale of the analyzing system is graduated directly to tenths of a circular degree and by means of observing microscopes reads directly to 0°.001. The microscopes are 180° apart, thereby correcting for any eccentricity of the circle.

An air bath with dimensions of 60 cm by 40 cm by 55 cm was placed between the polarizing and analyzing systems and mounted on separate supports to eliminate the possibility of disturbing the adjustments of the polariscope by opening and closing the door. The trough of the instrument passed through the end walls of the thermostat without touching them. There was thus a complete separation of thermostat and polariscope.

The thermostat was cooled below 20° C by ice water circulating through a copper coil and then heated to 20° C. The heating was accomplished by a wire coil wound on a separate frame with the same dimensions as the inside of the bath. The direction of the windings was such that any magnetic field produced was at right angles to the path of the light. Careful tests failed to

UNIV. OF CALIFORNIA

show the slightest magnetic rotation of the plane of polarization. The heating current was regulated by means of a toluene coil, a relay and a mercury contact interrupter. The temperature was controlled more closely than 0°05 C.

(*b*) THE LARGE THERMOSTAT.—The saccharimeter readings were made in a large thermostat with a content of about 15 cubic meters. The temperature regulation was very similar in principle to that already described above in connection with the polarimeter for absolute measurements. The air was chilled below 20° C by a brine coil. In order to obtain effective regulation at 20° C a thermostatic heater of 800 watts capacity was required. The capacity and regulation left little to be desired. With two observers in the thermostat the maximum variations were about 0°3 C.

(*c*) THE SACCHARIMETERS.—Three different makes of saccharimeters were used in order to eliminate the possibility of some peculiarity of the instrument construction affecting the measurements. They were a Bates type Fric, a Schmidt & Haensch, and a Julius Peters. Two instruments were used in each experiment, one of which was always the Bates type Fric.

The Bates type has been fully described[24] by one of us. It is sufficient for our purpose to note that the instrument used was a 200 mm double quartz-wedge compensating saccharimeter with transparent glass scales which could be read directly to 0°01 S. It was equipped with a thermometer graduated in fifths of a degree, which gave the temperature of the wedges. The optical system is shown diagrammatically in Fig. 7. This saccharimeter was inclosed in a wooden thermostat insulated with asbestos. The method of automatic temperature control was similar to that used on the thermostat described above in connection with the large polarimeter for absolute measurements. The maximum temperature variations were generally a few hundredths of a degree. In order to manipulate the quartz wedges the milled head was removed from the horizontal rod which shifted the wedges and replaced by a long shaft which passed through the wall of the thermostat. The outside end of the shaft was fitted with a lever, about 10 cm long, in order to secure the slow movement of the wedges necessary to utilize the high sensibility of the instrument.

---

[24] Bates, Bull. Bur. Standards, 4, p. 461 (1908).

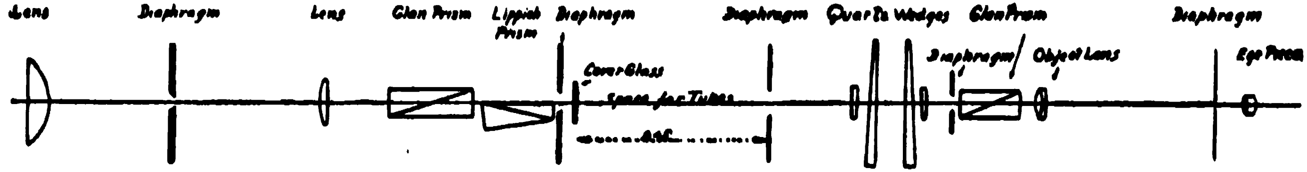


FIG. 7.—*Optical system of the Bates-Fric saccharimeter*

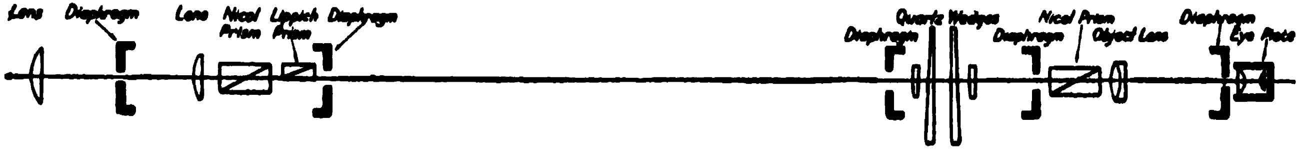


FIG. 8.—*Optical system of the Schmidt & Haensch saccharimeter*

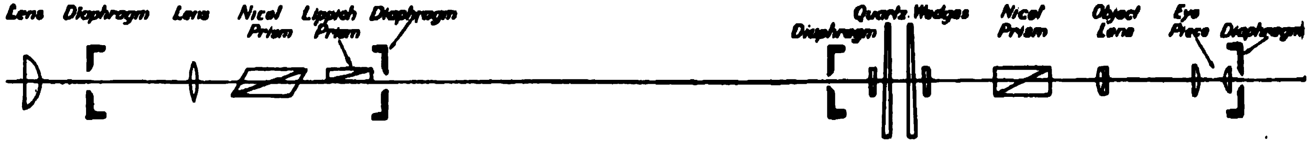


FIG. 9.—*Optical system of the Peters saccharimeter*

The Schmidt & Haensch saccharimeter was a modern instrument and an excellent example of the work of that firm. It had a double quartz-wedge compensation and a small but sensitive half-shadow field. The half-shadow angle of the Lippich polarizing system was about 6°. This saccharimeter accommodated tubes up to 600 mm in length. As it was not equipped with a thermometer giving the temperature of the wedges a hole was made in the metal case containing the analyzing system and a thermometer inserted with the bulb in proximity to the wedges. The arrangement of the optical system is shown in Fig. 8. The nickelin scales, being illuminated by reflected light, had a broad black line between verniers and scales. This fact, together with the width and irregular edges of the rulings, made it impossible to read the scales with an accuracy corresponding to that with which the settings could be made. The difficulty was overcome by resorting to the more laborious method of the micrometer microscope. The regular scale telescope of the saccharimeter was replaced by a microscope equipped with parallel cross hairs and rotating drum. The graduations on the drum were of a magnitude such that one division corresponded to a shift of the cross hairs of about 0°.01 S. In order to decrease the movement of the wedges corresponding to a given movement of the observer's hand a lever was attached perpendicular to the vertical drive rod which moved the wedges.

The Peters saccharimeter was an excellent instrument built for tubes up to 200 mm in length. It had a large and sensitive field. The Lippich polarizer had a half-shadow angle of about 6°. The optical system is shown diagrammatically in Fig. 9. The instrument was equipped with a thermometer giving the temperature of the wedges. The same difficulty was encountered in reading the nickelin scales as in the Schmidt & Haensch saccharimeter. It was overcome in the same way by the use of a suitable micrometer microscope. An additional lever was also found necessary in order to obtain a smaller movement of the quartz wedge. The instrument was tested on the basis of standardization adopted by the International Sugar Commission, at the Institut für Zucker-Industrie. The certificate showed that eight points on the positive wedge were checked against sugar solutions with a maximum error of 0°.02 S, the 87°.5 S and the 100° S points showing zero corrections.

6. LIGHT SOURCES

Two spectrum lines were utilized for the measurement of the rotations in circular degrees, namely, $\lambda = 5461$ Å and $\lambda = 5892.5$ Å. The former is the so-called "yellow-green" line of incandescent mercury vapor. Its many advantages for polarimetric work have already been described by one of us.[25] The lamps used were of quartz. These were fitted with special air-cooling apparatus, which permitted their operation at the high current densities necessary to give the desired intensity. The source $\lambda = 5892.5$ Å was obtained from the two sodium lines D_1 and D_2 by heating fused Na_2CO_3 in an oxyhydrogen flame. Both of these sources were carefully purified by means of an improved type of dispersive system which will be described by one of us in a subsequent paper. The purification secured was so perfect that with intensities sufficiently high to permit the use of a half-shadow angle of 3° for reading the solutions the field of the instrument was well illuminated and uniform in color.

The white light source used in the saccharimeter measurements was the same as that employed in the original Herzfeld-Schönrock research previously referred to and which gave the relation 100° S = 34°.657 for the value of the conversion factor. The light from a Welsbach mantle (Auerlicht) was passed through a 15 mm thickness of a 6 per cent solution of potassium bichromate before it entered the instrument. This method of modifying the character of the light was officially adopted by the International Congress for Uniform Methods of Sugar Analysis at the New York meeting[26] in September, 1912.

7. QUARTZ CONTROL PLATES

Two quartz plates, designated Nos. 1 and 3, were used throughout the measurements. Both are of excellent quality, optically homogeneous, nearly plane parallel and are primary standards of the Bureau of Standards. They have been tested at this Bureau, and at the Physikalisch-Technische Reichsanstalt, and in addition plate 1 has been tested at the Institut für Zucker-Industrie. A summarized statement of the values of the physical constants of these plates in our possession at the beginning of the research is given in Table 5. All the values given in sugar degrees are on the basis of standardization adopted by the International Sugar Commission. The values in the column headed "calculated" were obtained by using the Herzfeld-Schönrock conversion factor and the accepted value of the rotation in circular degrees. All rotation values are for 20°.

---

[25] Bates, Bull. Bur. Standards, 2, p. 239 (1906).

[26] Bryan, Am. Sugar Ind., Nov. 1912, p. 62. Zs. Ver. Zuckerind. 68, I, p. 29 (1913); Int. Sug. J., 15, p. 8 (1913).

TABLE 5

Physical Constants of Quartz Control Plates

Plate	Diameter	Axis error in degrees, P. T. R.	Rotation in circular degrees				Rotation in sugar degrees	
			λ=5892.5Å, B. S.	λ=5892.5Å, P. T. R.	λ=5892.5Å accepted value [27]	λ=5461Å, B. S.	Calculated	Inst. Zuck. Ind.
	mm							
1........................	15.6	0.052	34.597_8	34.596	34.596_9	40.662_6	99.827	99.82
3........................	16.0	0.037	34.629_3	34.626	34.627_6	40.697_3	99.915	....

[27] Bates, Bull. Bur. Standards, 2, p. 239 (1906).

In order to utilize the high sensibility of the large polarimeter it is necessary to take unusual precautions to insure that the axis of each polariscope tube and quartz plate be parallel to the axis of the optical system of the instrument. A simple calculation shows that in order to produce an increase of 0°.001 in the rotation angle between the axis of tube or plate and that of the instrument must be about 27 minutes. The eyepiece of the observing telescope was replaced with a Gauss ocular and the trough adjusted until the axes coincided within approximately 15 minutes. The maximum possible error due to this source was therefore of the order of 0°.0005.

8. POLARISCOPE TUBES

The polariscope tubes used were all of glass, similar in design and 200 mm in length. Preliminary experiments with 400 mm tubes read on the large polarimeter demonstrated the desirability of using the shorter tube. Two of the saccharimeters would not take the 400 mm tubes and it was advantageous in each experiment to read the same tube on both saccharimeter and polarimeter. In addition the short tube is easier to handle, it is not so difficult to keep the temperature of the liquid uniform throughout, and the definition of the polariscope field is considerably better.

All the tubes, Fig. 6, were of the water-jacketed type. Owing to the fact that air-bath thermostats were used it was unnecessary to flow water through the metal jacket to maintain the temperature of the tube at 20°. A side tube with a 10 mm opening extended into the tube proper. The flared outer end of the side tube carried a glass stopper through which a thermometer, fitted to the stopper by a ground joint, extended into the body of the solution. A capillary opening in the stopper eliminated any undue pressure on the cover glasses and consequent danger of double refraction. The cover glasses were carefully selected and were fairly free from internal strains. Inasmuch as the measurements were all made at one temperature, practically no difficulty was experienced in preventing leakage around the cover glasses. No adhesive or cement was necessary to prevent evaporation. The lengths (Table 6) were determined by D. R. Miller of the division of weights and measures. Inasmuch as the rotation measurements necessarily extended over a considerable period of time, the lengths were redetermined after an interval of about one year. Both determinations were in good agreement. The values accepted were each the average of two series of observations, one series being taken on the rim and the other with the cover glasses in place.

TABLE 6

Lengths of Polarization Tubes, with Corrections for Normal Solution

Tube number	Length in millimeters at 20° C	Corrections in degrees sugar	Corrections in circular degrees λ=5461 Å
8819A	199.945±.005	+0.028	+0.011
8819B	199.952±.005	+ .024	+ .010
7294A	199.984±.005	+ .008	+ .003
5797A	200.025±.005	− .013	− .005

9. ROTATION PRODUCED BY POLARISCOPE TUBES FILLED WITH WATER

Any change in the general appearance of a photometric field is likely to cause a difference between the settings before and after the change. The magnitude of this difference varies with the individual. It is thus of great importance in measuring the absolute rotation of a substance to insure that no change in the appearance of the field occurs between the determination of the zero point and the tube reading. The apparent total rotation of a tube of solution may thus consist of the rotation due to the active solution plus or minus a small apparent rotation due to the changed appearance of the field. The latter may be due to a number of causes, among which may be mentioned slight double refractions, lens effects, etc. Obviously the most effective method of elimination is to determine the zero point with the tube filled with the inactive solvent. Owing to the fact that it was necessary to have the tubes dry before filling with solution it was impracticable to do this. An investigation was therefore made of the change in the zero point by a tube filled with distilled water. In many instances after the observations on the sugar solutions had been made the tubes were thoroughly cleansed without removing the cover glasses, filled with distilled water, and read. A series of experiments on two tubes is given in Table 7.

TABLE 7

Rotation by Tubes Filled with Water

Tube 7294A	Tube 8819A
Degrees	Degrees
−0.0015	−0.0002
−0.0020	0.0000
−0.0043	+0.0001
+0.0003	−0.0013
−0.0013	−0.0009
....	−0.0023
0.0000	0.0000
Av. −0.0015	Av. −0.0007

In the measurements on the normal solutions the zero point was determined without the use of the tube, and from an inspection of the data in Table 7 it is very questionable whether any increase in the accuracy of our measurements could be made by a zero correction obtained by reading the tube filled with water. We have therefore in the present investigation assumed that the total rotations measured were due solely to the sucrose.

IV. OBSERVATIONS AND COMPUTATIONS

1. SACCHARIMETER VALUES OF QUARTZ CONTROL PLATES

In order to determine the agreement among the three saccharimeters and the average deviation from the Herzfeld-Schönrock values, as well as for use in the calculations in the present investigation, a series of plate readings were made. The data are summarized in Table 8. Each value is the average of two series of readings by independent observers. In taking the readings the procedure was to make six settings on the zero point followed by six settings on the plate and four on the zero. The agreement between the average values for the three different makes of instruments is very satisfactory, and is an excellent illustration of the degree of perfection attained in the modern saccharimeter. From Table 5 the sodium values of plates 1 and 3 are 34°.597 and 34°.628, respectively. Since the Herzfeld-Schönrock value gives 0°.34657 = 1° S, we obtain 99°.827 S for the value of plate 1 and 99°.915 S for plate 3. From Table 8 the grand average for plate 1 is $99^{\circ}.80_{6}$ S and $99^{\circ}.88_{2}$ S for plate 3. The average difference between the observed and the theoretical values is thus $0^{\circ}.02_{7}$ S. It is therefore evident that these modern saccharimeters give an average reading which is $0^{\circ}.02_{7}$ S lower than they should if accurately standardized on the Herzfeld-Schönrock value so as to conform to the basis of the International Sugar Commission. A similar calculation using the old equation,[28] 0°.3469 = 1°, shows these saccharimeters give an average reading which is $0^{\circ}.06_{7}$ S higher than the Ventzke basis of standardization.

---

[28] Landolt, Das Optische Drehungsvermögen 2 Auflage, p. 337 (1898).

TABLE 8

Saccharimeter Readings on Quartz Plates

Plate 1 (Herzfeld-Schönrock value—99°827 S)			Plate 3 (Herzfeld-Schönrock value—99°915 S)		
Bates-Fric	Schmidt & Haensch	Peters	Bates-Fric	Schmidt & Haensch	Peters
99°82	99°81	99°81	99°91	99°96	99°88
.85	.81	.80	.89	.84	.87
.81	.80	.81	.88	.86	.88
.82	.81	.79	.89	.88	.88
.80	.79	.79	.89	.84	.86
.78	.82	....	.86	.87	....
.77	.82	....	.86	.88	....
.82	.80	....	.88	.94	....
.82	.82	....	.88	.89	....
.78	.82	....	.93	.88	....
.81	.80	....	.91	.88	....
.79	....	....	.86	....	....
.81	....	....	....	....	....
Av. $99^{\circ}80_{6}$	$99^{\circ}80_{9}$	$99^{\circ}80_{0}$	$99^{\circ}88_{7}$	$99^{\circ}88_{4}$	$99^{\circ}87_{4}$

Grand average for plate 1 .... $99^{\circ}80_{5}$
Grand average for plate 3 .... $99^{\circ}88_{2}$

Average instrument error, Bates-Fric .... $0^{\circ}02_{4}$ S
Average instrument error, Schmidt & Haensch .... $0^{\circ}02_{4}$
Average instrument error, Peters .... $0^{\circ}03_{4}$

Average .... $0^{\circ}02_{7}$

2. $\frac{\phi^{20}{}_{\lambda=5892.5\,Å}}{\phi^{20}{}_{\lambda=5461\,Å}}$ FOR THE NORMAL SUCROSE SOLUTION

The ratio of the rotations of quartz for λ = 5461 Å and λ = 5892.5 Å being known with a high degree of precision it is desirable for use in the present investigation as well as for other purposes to establish a similar ratio for sucrose. Since the constant to be determined is a ratio it is unnecessary to prepare exactly normal solutions for the experiments, although the solutions used were very nearly normal. The sucrose was taken from a selected sample of known purity. Seven complete experiments were made. Two tubes, described above, were measured in each experiment, a complete set of observations being taken by two independent observers. Since it is of great importance to maintain the physical condition of the tubes constant throughout each experiment the temperature was carefully controlled at 20° C and the observations completed on the same day they were begun. In addition the light sources were so arranged that the shifting from one to the other was made with but little loss of time, thus eliminating the possibility of a change in the condition of the solution. Ten zero point and ten tube settings were made by each observer for each light source. The data are summarized in Table 9. We have therefore

$$\frac{\phi^{20}_{\lambda=5892.5\ \text{Å}}}{\phi^{20}_{\lambda=5461\ \text{Å}}}=0.84922 \qquad (3)$$

TABLE 9

Value of $\frac{\phi^{20}_{\lambda=5892.5\ \text{Å}}}{\phi^{20}_{\lambda=5461\ \text{Å}}}$ for Sucrose

Experiment	$\varphi^{20}_{\lambda=5461\ \text{Å}}$, circular degrees	$\varphi^{20}_{\lambda=5892.5\ \text{Å}}$, circular degrees	$\frac{\varphi^{20}_{\lambda=5892.5\ \text{Å}}}{\varphi^{20}_{\lambda=5461\ \text{Å}}}$
1	40.7772	34.6349	0.84937
2	40.7761	34.6239	.84912
3	40.7860	34.6357	.84921
4	40.5044	34.3975	.84923
5	40.5207	34.4073	.84913
6	40.9978	34.8163	.84922
7	41.0110	34.8297	.84928
Average			.84922±.00002

Subsequent to the determination of the similar ratio for quartz made by one of us, a redetermination of this constant was made with the assistance of Francis P. Phelps, on the apparatus used in the present research and the value 0.85076 was obtained, the original determination giving 0.85094. Taking the average of these we obtain

$$\frac{\phi^{20}_{\lambda=5892.5\ \text{Å}}}{\phi^{20}_{\lambda=5461\ \text{Å}}}=0.85085 \qquad (4)$$

We thus have 0.00163 as the difference between 0.85085 and the above value for sucrose. The quantity 0.00163 is due to the difference between the rotary dispersion curves of quartz and sucrose in this portion of the spectrum, thereby producing color effects in the field of the quartz-compensating saccharimeter when a white light source is used and necessitating the adoption of the potassium bichromate filter.

3. CORRECTIONS FOR TEMPERATURE

The temperature corrections in polarimetric work are unusually complicated. In precision measurements it is therefore desirable to keep all corrections as small as possible. Fortunately the standardization temperature of 20° C being practically room temperature, greatly facilitates this. The specific rotation coefficient for quartz is 0.000136. The linear coefficients of expansion parallel and perpendicular to the optic axis and for the nickelin scales used on quartz wedges are 0.000007, 0.000013, and 0.000018, respectively. Thus the total temperature coefficient for the ordinary saccharimeter is

$$0.000136+0.000007-0.000013+0.000018=0.000148 \qquad (5)$$

If the scale be of glass, 0.000008 must be substituted for 0.000018 and the right-hand member of (5) becomes 0.000138. Since the effect of the expansion coefficient 0.000148 is to lower the reading of the scale with an increase of temperature, the apparent polarization of any substance is lower than it should be and the reading at 20° (S_{20}) is given by the following:

$$S_{20}=S_t+S_t\,0.000148\,(t-20) \qquad (6)$$

When a quartz control plate is read in a saccharimeter this effect is not completely compensated. The temperature coefficient of the plate is

$$0.000136+0.000007=0.000143 \qquad (7)$$

The reading (W_{20}) of the plate is then

$$W_{20}=W_t+W_t\,0.000005\,(t-20) \qquad (8)$$

where *t* is the temperature of the wedges. The correction given by (8) changes sign if the scale be of glass.

When a normal sucrose solution is polarized in a glass tube the linear expansion coefficient of the tube is 0.000008. The temperature coefficient of the specific rotation at 20° C for the normal sucrose solution ($p = 23.701$) has been given by Schönrock as 0.000184. The expansion coefficient of the solution is 0.000285. The temperature coefficient for tube and solution is thus

$$-0.000008 + 0.000184 + 0.000285 = 0.000461 \qquad (9)$$

and the reading of the solution at 20° C (R_{20}) is given by

$$R_{20} = R_t + R_t\, 0.000461\ (t-20) \qquad (10)$$

4. DETERMINATION OF THE READING OF THE NORMAL SOLUTION ON THE HERZFELD-SCHÖNROCK SCALE

In order to check the accuracy of the Herzfeld-Schönrock scale 10 complete experiments, numbers 25 to 34, inclusive, were made in the final series of measurements. Two 200-mm tubes of solution were used in each experiment, with the exception of number 26, in which one tube was lost. The solutions were prepared as described above. The fact that no attempt was made to prepare accurately normal solutions was of advantage in that the observers could be in no degree prejudiced by a foreknowledge of what the instrument reading should be. Only after the experimental work was completed and the correction for the concentration applied was the reading of the normal solution known. If the Herzfeld-Schönrock values for the international commission's basis of standardization are correct, then our solutions, when corrected for concentration, should read 100° S on the saccharimeter within the limits of the experimental error.

The data describing the solutions used in the final series of measurements are given in Table 10. In each experiment the solutions were made up to volume and all observations completed on the same day. Each of the two tubes was read by two observers on two saccharimeters. When the tubes were first placed in a thermostat they were allowed to remain at least two hours before reading, in order to bring solution and air to the same temperature. In experiments 25 and 26 no plate readings were taken. Not less than six zero-point settings were made, followed by not less than six tube settings and four more zero-point settings. The second tube was then read, and finally not less than six additional zero-point settings made. In experiments 27 to 34, inclusive, the zero points were not read. Instead six readings were taken on plate 1, followed by eight readings on a tube of solution, six readings on plate 3, and eight on the second tube of solution. The temperatures of the air bath, the solution, and the wedges were taken at the beginning and end of each set of six or eight observations. A complete record was thus secured of the temperature conditions throughout each experiment. Owing to the excellence of the thermostats, we were able to make our measurements at a practically constant temperature, which seldom differed from 20° C by more than 0°.2 C. The corrections to be applied were therefore small.

In the present investigation all solutions were made up to volume at 20° C. In order to obtain the rotation on the saccharimeter, it is then necessary to correct the reading for the temperature difference between 20° C and the solution temperature and 20° C and the quartz-wedge temperature. The instrument correction was obtained from (6) (t being the temperature of the wedges) and seldom exceeded 0°.003 S. No distinction was made between the corrections for glass and nickel in scales. Similarly, in reading the quartz plates, equation (8) was ignored owing to the fact that the correction was negligible. The correction for the solution is given by (10). The magnitude of this correction rarely exceeded 0°.01 S.

The agreement between the readings of the individual observers for the final series of measurements is shown in Table 11. While it is true that all difference in color between the two halves of the field of a saccharimeter is not eliminated by the use of the bichromate cell, yet the elimination must be fairly complete as indicated by the agreement between the readings. This is in accord with the results obtained by Schönrock[29] who has made an investigation of this important point.

The saccharimeter readings for the normal solutions are given in Table 12. In experiments 25 and 26 the rotation is the difference between the zero point and the tube reading after adding the scale correction from Table 4. In the remaining experiments

---

[29] Loc. cit.

TABLE 10

Data on the Preparation of the Solutions

Experiment	Designation	Weight of sugar (air, brass weights)	Weight of solution (air, brass weights)	Sugar by weight in vacuo	Density, K.N.E.K. tables	Volume of solution	
						Computed from weights and density	By flask mark
1	2	3	4	5	6	7	8
		g	g	Per cent		cc	cc
25	Fraction 27	24.370_8	101.570	23.986_8	1.09891	92.514	92.518
26	Fraction 27	26.207_3	109.497	23.926_1	1.09863	99.761	99.750
27	Fraction 27	34.052_8	142.665	23.861_6	1.09834	130.010	130.012
28	Sample C	24.029_2	101.546	23.655_7	1.09741	...	...
29	Fraction 30	23.856_8	101.381	23.523_8	1.09680	92.518	92.520
30	Fraction 32	34.018_8	142.636	23.841_9	1.09825	130.000	129.997
31	Fraction 31	24.181_1	101.496	23.817_0	1.09814	...	...
32	Fraction 31	26.003_8	109.533	23.732_4	1.09775	...	...
33	Sample A	34.326_1	143.045	23.988_7	1.09892	...	...
34	Sample B	25.881_3	109.610	23.604_5	1.09717	...	...

TABLE 11

Agreement Between Individual Observers with Use of Bichromate Light Filter

Experiment	Bates-Fric		Schmidt & Haensch		Peters	
	Observer A	Observer B	Observer A	Observer B	Observer A	Observer B
	Degrees	Degrees	Degrees	Degrees	Degrees	Degrees
25	99.908	99.891	...	99.903	...	...
26	99.916	99.902	99.852	99.852	...	...
27	99.872	99.874	99.870	99.905	...	...
28	99.874	99.883	[a] 99.912	99.894	...	...
29	99.893	99.872	...	...	99.859	99.854
30	99.920	99.937	...	...	99.890	99.928
31	99.863	99.884	...	...	99.885	99.909
32	99.901	99.898	...	...	99.965	99.884
33	99.896	99.907	...	...	99.915	99.887
34	99.905	99.896	...	...	99.878	99.900
Mean	99.895	99.895	99.876	99.889	99.899	99.894

[a] Solution observed in only one polariscope tube.

TABLE 12

Reading of the Normal Solution on the Saccharimeter

Experiment	Average rotation of solution for two saccharimeters, degrees sugar	Rotation of normal solution on the saccharimeter, degrees sugar			
		Bates-Fric	Schmidt & Haensch	Peters	Average
1	9	10	11	12	13
25	101.19_3	99.90_9	99.90_8		99.90_8
26	100.89_6	99.90_9	99.85_3		99.88_9
27	100.61_4	99.87_5	99.88_9		99.88_3
28	99.68_7	99.88_1	99.90_6		99.89_3
29	99.04_4	99.88_5		99.85_8	99.87_6
30	100.56_9	99.93_0		99.91_1	99.92_1
31	100.41_8	99.87_6		99.89_9	99.88_8
32	100.05_1	99.90_3		99.92_7	99.91_4
33	101.23_3	99.90_4		99.90_3	99.90_4
34	99.43_6	99.90_8		99.89_1	99.89_7
Average		$99^\circ 89_7$ S	$99^\circ 88_7$ S	$99^\circ 89_2$ S	$99^\circ 89_6$ S

the total instrument correction, including the zero-point error, is found by subtracting the Herzfeld-Schönrock values of plates 1 and 3 from the readings of these plates in each experiment. The value obtained when this correction is added to the tube reading gives the actual reading of that tube on the Herzfeld-Schönrock scale. This method, which is much used in polarimetric measurements when a plate of known value can be used to eliminate errors due to instrument and light source, obviates the necessity of reading the zero point. It also eliminates as far as possible the question of any error due to a change in the instrument correction.

The final correction to be applied to the tube reading is that for concentration. Inasmuch as we may assume that the rotation is directly proportional to the concentration we have

$$R=\frac{CR'}{C'} \qquad (11)$$

where R and C are the rotation and concentration of the normal solution and R' and C' the rotation and concentration of a near normal solution. From the definition of the normal solution C is 26 grams, and as all weighings were corrected to vacuo it becomes 26.0159. R' is the observed saccharimeter reading.

$$\text{Obviously } C' = 100 \; \frac{\text{Weight of sugar in vacuo}}{\text{Volume of solution.}}$$

$$= 100 \; \frac{\text{Weight of sugar in vacuo} \times \text{density of solution}}{\text{Weight of solution in vacuo.}}$$

We thus have

$$R = 0.260159 \; \frac{R' \text{ (Weight of solution in vacuo)}}{\text{(Density of solution) (Weight of sugar in vacuo)}} \qquad (12)$$

Equation (12) was applied to the rotation of each tube as measured by each observer, giving four values for the rotation of normal solution on each saccharimeter in each experiment. The rotations given in columns 10, 11, and 12, Table 12, are the averages of these four values. Column 9 shows the rotations actually measured. The values in column 13 show the rotation of the normal solution on the Herzfeld-Schönrock scale for each experiment. It will be observed that the agreement of the determinations for the different saccharimeters as well as that between the individual experiments is very satisfactory and that in no instance did the rotation of a normal solution even approximate 100° S. The average of column 13 is $99\overset{\circ}{.}89_5$ S. We therefore conclude that the Herzfeld-Schönrock scale is in error by $0\overset{\circ}{.}10_5$ S; and that the ordinary saccharimeter, inasmuch as its wedges are calibrated to that scale, gives readings for polarizations in the neighborhood of 100° S that are $0\overset{\circ}{.}10_5$ S too low.[30]

5. THE ABSOLUTE ROTATION OF THE NORMAL SOLUTION FOR THE MERCURY LINE, $\lambda = 5461$ Å

On the same day that each of the saccharimeter measurements given in Table 12 was made the solutions were read in the large polarimeter to obtain the rotation of the normal solution for the polarimetric standard light source, the so-called yellow-green line of incandescent mercury vapor, λ = 5461 Å. When the tubes were placed in the instrument ample time was allowed for the solution to come to the temperature of the thermostat. This was done because the thermometer in the solution was not read. Instead the temperature of the air in the immediate vicinity of the tube was taken.

---

[30] Subsequent to the presentation of our preliminary paper at the Eighth International Congress of Applied Chemistry, Walker checked our value for the reading of the normal solution on the saccharimeter. (See Sugar, 17, No. 2, p. 47 (1915). He prepared sucrose by the alcohol method and obtained $99\overset{\circ}{.}88$ S. He also read a standard sample issued by the Bureau of Standards and obtained $99\overset{\circ}{.}90$ S. It is important to note that a careful experimenter with average laboratory facilities obtains results in agreement with the value given in Table 12.

TABLE 13

Rotation of Normal Solution for λ=5461 Å

Experiment No.	Rotation λ=5461 Å	Experiment No.	Rotation λ=5461 Å
	Degrees		Degrees
25	40.757	31	40.749
26	40.770	32	40.769
27	40.761	33	40.771
28	40.763	34	40.767
29	40.751		
30	40.773	Average	40.763

Each of the two tubes was read by two observers. Each observer made not less than six readings on the zero point, alternating with right and left eyes. The temperature was then taken and not less than six readings made on the tube of solution, temperature taken, and not less than six zero-point readings made. Temperature was then taken and the second tube read. Temperature was again taken and six additional zero-point readings made. The scale readings were equally divided between the two reading telescopes, 180° apart, in order to correct for any eccentricity of the circle. In general, the zero-point readings immediately preceding and following the tube readings were taken to determine the zero point for that tube. The effect of any possible shift in the zero point such as might arise from a change in the illuminating system is thus eliminated. In making the corrections for the temperatures of the solutions (24) was used. The temperature of the thermostat was maintained so nearly at 20° that the magnitude of the correction was seldom 0°.002. The results of the measurements are given in Table 13. In the development of polarimetric measurements at the Bureau of Standards a number of different methods of purification for intense monochromatic sources have been experimented with. The two systems finally adopted show a small unexplainable difference in the rotations obtained. We have therefore made a correction of $0\overset{\circ}{.}004$ to the rotations actually measured so that our values are what we would have obtained had the solutions been measured with both dispersive systems. The rotation of the normal solution, column 2, correcting for concentration, was obtained from (12). Taking the average value for the 10 experiments we obtain

$$\begin{gathered}\text{Normal sugar solution} = 100^\circ \text{ sugar} = \\ 40\overset{\circ}{.}763\ (\lambda = 5461\ \text{Å})\ \text{at}\ 20^\circ\ \text{C}\end{gathered} \tag{13}$$

6. THE ABSOLUTE ROTATION OF THE NORMAL SOLUTION FOR THE SODIUM LINES, λ=5892.5 Å

In Table 9 the ratio of the rotations of the near-normal sucrose solution for λ = 5892.5 Å and λ = 5461 Å is shown to be 0.84922. The rotation of the normal solution for λ = 5461 Å being $40\overset{\circ}{.}763$ we have

$$\begin{aligned}\text{Normal sugar solution} = 100^\circ\ \text{sugar} &= 40\overset{\circ}{.}763 \times 0.84922 \\ &= 34\overset{\circ}{.}616_7\ (\lambda = 5892.5\ \text{Å})\ \text{at}\ 20^\circ\ \text{C}\end{aligned} \tag{14}$$

as the absolute rotation of the normal solution for the sodium lines.

7. DETERMINATION OF THE CONVERSION FACTOR

The value of the conversion factor has been determined by two methods of calculation, both of which are wholly independent of the data obtained by previous investigators. In both methods the tubes of solution are used to make an independent calibration of the wedges of the saccharimeters in each experiment. Inasmuch as the same fundamental data are used in each procedure, the object in determining the conversion factor by two methods is to secure a positive check on the final value for each experiment.

From the definition of the conversion factor previously given we have

$$\text{Conversion factor} = \frac{100\ \text{rotation of plate in circular degrees}}{\text{Rotation of plate on true saccharimeter scale}} \tag{15}$$

Since the rotations of plates 1 and 3 in circular degrees are known from Table 5, it is only necessary to determine the rotation of the plates on the true saccharimeter scale as determined by our normal solutions.

The first method is the more direct of the two. The conversion factor is calculated for each experiment entirely from the data secured during that experiment. This has been accomplished by calculating directly the correction which must be applied to the saccharimeter reading in order that the normal solution shall read 100° S on that scale. All the errors involved in the instrument error, such as zero and scale errors, are automatically eliminated. The correction for each experiment is thus obtained, which must be applied to the quartz-plate readings taken during the experiment to find the values of the plates on the true scale. The latter must be known in order to calculate the conversion factor. We have therefore

$$100^\circ \text{ S (true scale)} = (\text{Reading of solution} \pm \text{instrument correction})\ (\text{concentration factor}) \qquad (16)$$

or

$$\text{Instrument correction}^{31} = \text{Reading of solution} - \frac{100}{\text{Concentration factor}} \qquad (17)$$

In this method advantage is taken of the fact that the true scale and the Herzfeld-Schönrock scale differ by only 0°.1 S at the 100° points. It thus becomes possible to use quartz plates whose sugar values differ to a considerable degree from that of the true normal quartz plate without appreciable error due to the difference in the units of the two scales. Plate 3, with a value of 99°.915 on the Herzfeld-Schönrock scale is very nearly a normal plate for the true scale, and plate 1, with a value of 99°.827 differs by less than 0°.1 S from a true normal plate. The maximum possible error in the value of the rotation of plate 1 on the true scale is therefore of the order of 0°.0001 S and is negligible. The instrument correction given by (17) is applied to the quartz-plate readings secured in each experiment to obtain the values of the plates on the true saccharimeter scale. The conversion factor is then calculated from (15).

---

[31] Instrument correction here includes zero displacement as well as the errors in the scale graduation.

In the second method the scale readings on plates 1 and 3 in each experiment are averaged. The difference between this value and the averages for the two saccharimeters used, given in Table 8, gives the zero correction. The correction is applied to the tube readings giving the observed rotation of the solution. The correction for concentration is then made by equation (12) which gives the rotation of the normal solution. This value would have been 100° S on a true scale. We have, therefore, using the observed plate rotation from Table 8,

Rotation of plate on true scale

$$= \frac{100 \text{ (Observed rotation of plate)}}{\text{(Reading of normal solution)}} \qquad (18)$$

The conversion factor is then calculated from (15).

Although the procedure in this method differs from that indicated in the preceding and a zero-point correction is necessary, it should be noted that any possible error in the determination of the zero point due to the use of the plate values from Table 8, can not enter into the value for the plate rotation on the true scale. Obviously from (18) the desired value is a ratio. Since any error made in determining the zero point is present in both the numerator and the denominator of (18), it is not essential to know the plate readings from Table 8 to an accuracy greater than will affect the value of the sixth figure in the ratio. In this method as well as in the first method no accurate determination of the zero point is essential and the number of saccharimeter readings in each experiment necessary to the determination of the conversion factor is reduced to the minimum.

The values of the conversion factor by the first method are given in Table 14. The procedure indicated above for that method was modified in using the data from experiments 25 and 26. Since the zero was directly determined the scale correction was calculated by using the instrument correction from (17), and added to the plate values from Table 8 in order to obtain the reading of the plates on the true scale. The accuracy of the values from experiments 25 and 26 are dependent on a series of saccharimeter plate readings extending over a period of some months. Thus, the agreement between experiments 25 and 26 and the remainder of the series is an excellent illustration of the reliability of the modern saccharimeter over considerable intervals of time. The values obtained by Method II are identical with those given in Table 14 and are therefore omitted.

The average of column 5 in Table 14 is $34^{\circ}620_1$ and the corresponding value calculated by Method II is $34^{\circ}620_2$. The final average value is therefore $34^{\circ}620_2$, and we have

Normal quartz plate $= 100^{\circ}$ S $= 34^{\circ}620$ ($\lambda = 5892.5$ Å) at 20° C (19)

1° S $= 0^{\circ}34620$ ($\lambda = 5892.5$ Å) at 20° C (20)

$2^{\circ}8885_0$ S $= 1^{\circ}$ ($\lambda = 5892.5$ Å) (21)

TABLE 14

Determination of Conversion Factor by Method I

Experiment	Average reading of solution on saccharimeters, sugar degrees	Conversion factor (circular degrees)					
		λ=5892.5 Å			λ=5461 Å		
		Plate 1	Plate 3	Average	Plate 1	Plate 3	Average
1	2	3	4	5	6	7	8
25..........	101.31	34.620_1	34.623_8	34.622_0	40.690_3	40.694_6	40.692_5
26..........	101.09	$.614_3$	$.617_1$	$.615_7$	$.683_4$	686_8	$.685_3$
27..........	100.91	$.605_3$	$.622_4$	$.613_8$	$.672_7$	$.691_8$	$.682_4$
28..........	100.02	$.617_0$	$.617_9$	$.617_5$	$.686_5$	$.686_5$	$.686_5$
29..........	101.68	$.608_5$	$.616_9$	$.612_7$	$.677_6$	$.685_3$	$.681_5$
30..........	103.20	$.626_3$	$.629_7$	$.628_0$	$.697_5$	$.700_3$	$.698_9$
31..........	103.05	$.620_4$	$.618_3$	$.619_4$	$.690_3$	$.686_3$	$.688_3$
32..........	102.72	$.619_5$	$.634_9$	$.627_2$	$.689_8$	$.706_4$	$.698_1$
33..........	103.92	$.625_0$	$.621_7$	$.623_4$	695_9	$.691_3$	$.693_6$
34..........	102.13	$.621_1$	$.621_7$	$.621_3$	$.691_4$	$.691_0$	$.691_2$
Average.	....	....	....	$34.620_1 \pm 0.0012$	....	....	$40.689_8 \pm 0.0013$

The average of column 8 in Table 14 is $40^{\circ}689_8$ and the corresponding value calculated by method II is $40^{\circ}689_9$. The final average value is therefore $40^{\circ}689_9$ and we have

Normal quartz plate $= 100^{\circ}$ S $= 40^{\circ}690$ ($\lambda = 5461$ Å) at 20° C (22)

1° S $= 0^{\circ}40690$ ($\lambda = 5461$ Å) at 20° C (23)

$2^{\circ}4576_1$ S $= 1^{\circ}$ ($\lambda = 5461$ Å) (24)

8. DIFFERENCE IN CIRCULAR DEGREES BETWEEN THE NORMAL QUARTZ PLATE AND THE NORMAL SOLUTION

The rotation of the normal solution for sodium light is, from equation (14), 34°617, and of the normal quartz plate is 34°620 from (19). The rotation of the plate thus differs by only 0°003 from that of the solution, and no great error would have been made had previous investigators used the rotation of the normal solution for sodium light as the conversion factor. This condition no longer holds when $\lambda = 5461$ Å is used for the absolute rotations. From (13) the rotation of the normal solution for that source is 40°763, and from (20) 40°690 for the plate. The rotation of the solution is thus 0°073 larger than the plate. These differences being of opposite sign indicate that the rotary dispersion curves of the normal solution and normal plate, at 20° C, have a point in common. A calculation based on the above data and using the ordinary dispersion formulæ for quartz and sucrose fixes the crossing point at approximately $\lambda = 0.585\ \mu$. The normal quartz plate might thus be defined as one which has the same rotation in circular degrees as the normal sugar solution for $\lambda = 0.585\ \mu$. We do not consider it safe, however, to lay too much stress on this definition. The rotation difference of 0°003 is of nearly the same magnitude as the experimental error of the measurements. The question of the actual crossing can be settled only by making an accurate experimental determination of the curves.

9. CALCULATED DIFFERENCE IN SUGAR DEGREES, FOR NORMAL SOLUTION, BETWEEN WHITE LIGHT WITH BICHROMATE FILTER AND $\lambda = 5892.5$ Å

Owing to the difference in the rotation dispersion curves of sugar and quartz it is obvious that, although by definition the normal solution and plate both read 100° S on the saccharimeter with white light and bichromate filter, they may not have the same rotation when the light source is $\lambda = 5892.5$ Å. In that event the setting of the instrument for the normal solution must be changed to secure a match. From (14) and (19) this change amounts to −0°003 or using (21) −0°009 S. The normal solution will therefore read 99°99 S for $\lambda = 5892.5$ Å. The work of previous investigators indicates that the saccharimeter reading for sodium light is slightly higher than 100° S. Schönrock,[32] after a careful experimental determination, gives 100°.03 S as the reading of the normal solution for sodium light.

10. ROTATION DIFFERENCE, IN SUGAR DEGREES, FOR NORMAL SOLUTION BETWEEN λ=5461 Å AND λ=5892.5 Å

Owing to the constantly increasing use of the source λ = 5461 Å it is important to know the reading of the normal solution on the saccharimeter with this source as compared with sodium and white light. We know from (14) that when the normal solution is read in the saccharimeter with sodium light the rotation of the plane of polarization is 34°.617. This value is therefore the negative rotation of that thickness of the quartz plate which compensates when the wedge is shifted to give a match. If the source is changed to λ = 5461 Å the rotation of the solution is 40°.763 from (13), and that of the plate, using (4), is

$$\frac{34^\circ\!.617}{0.85085} = 40^\circ\!.685 \qquad (25)$$

The rotation of the plate is now 0°.078 less than that of the solution. This difference, using (24) is 0°.192 S and the thickness of the compensating plate must be increased by shifting the wedge that amount. We have therefore

$$\text{Saccharimeter reading}_{\lambda=5461\,\text{Å}} - \text{saccharimeter reading}_{\lambda=5892.5\,\text{Å}} = 0^\circ\!.19_2\,\text{S} \qquad (26)$$

Since the reading of the normal solution for λ = 5892.5 Å is 99°.99 S the reading for λ = 5461 Å is 100°.18 S.

The results of an experimental study of this difference is given in Table 15. The readings were taken by two independent observers. The sodium and mercury light sources were purified spectroscopically; and the apparatus was so arranged that the shift from one light source to the other could be quickly made. The average difference obtained was 0°.185 S. This value is in agreement with the calculated value of 0°.192 S. Schönrock [33] as the result of an experimental determination gives 0°.117 S for the right-hand member of (26); whereas by calculation, using the ratios for sugar and quartz for the two wave lengths, he obtains 0°.188 S.

---

[32] Schönrock Zs. Ver. Zuckerind., 54, p. 552 (1904).

[33] Loc. cit.

TABLE 15

Rotation Difference, Normal Solution, for Na and Hg Sources

$\phi_{\lambda=5461 Å} - \phi_{\lambda=5892.5 Å}$. Difference in sugar degrees]

Saccharimeter 1	Saccharimeter 2
0.14	0.25
.19	.22
.11	.25
.17	.19
.11	.23
.16	.18
Av. .15	.22

Grand average, both saccharimeters, 0.18_5.

11. THICKNESS OF THE NORMAL QUARTZ PLATE

Inasmuch as we have found the value of the conversion factor, in the rotation of the normal quartz plate, to be 34°620 for λ = 5892.5 Å and 40°690 for λ = 5461 Å, the old value of 1.5958 mm for the thickness of the normal plate is no longer applicable. Gumlich[34] as the result of a painstaking investigation, found the rotation of 1 mm of quartz for λ = 5892.5 Å, the light, travelling parallel to the optic axis, to be 21°7182 ± 0.0005 at 20° C. Recently Lowry[35] has made a number of measurements on the rotation of quartz and finds at 20° C 21°7283 per mm for sodium light, and 25°5371 per mm for λ = 5461 Å. The values of the thickness of the normal plate calculated from the above data are given in Table 16. The agreement between the second and third values in column 4 is very satisfactory in view of the fact that two independent values of the rotation per mm are used. The agreement between Gumlich's and Lowry's values for sodium light is not satisfactory.

TABLE 16

Thickness of the Normal Quartz Plate in Millimeters

Wave length of light source 1	Rotation of normal plate 2	Rotation of 1 mm of quartz at 20° C; light parallel to optic axis 3	Thickness of normal plate 4
			mm
5892.5 Å	34°620 (Bates & Jackson)	21°7182 (Gumlich)	1.5940
5892.5 Å	34°620 (Bates & Jackson)	21°7283 (Lowry)	1.5934
5461. Å	40°690 (Bates & Jackson)	25°5371 (Lowry)	1.5934

---

[34] E. Gumlich, Wiss. Abh. der Physikalisch-Technischen Reichsanstalt, **2**, p. 201 (1895); Zs. Instrk., p. 97 (1896).

[35] Lowry, Phil. Trans., **212**, p. 288 (1912–13).

12. THE SPECIFIC ROTATION OF SUCROSE

The rotation of the normal solution for $\lambda = 5892.5\,Å$ is 34°617 from (14) and for $\lambda = 5461\,Å$ is 40°763 from (13). Since this solution contains 26.016 g of sugar, weighed in vacuo, in 100 cc, at 20° C, we have

$$\left[\alpha\right]^{20}_{\lambda=5892.5\,Å} = \frac{100 \times 34.617}{2 \times 26.016} = 66^\circ529 \tag{27}$$

and

$$\left[\alpha\right]^{20}_{\lambda=5461.\,Å} = \frac{100 \times 40.763}{2 \times 26.016} = 78^\circ342 \tag{28}$$

Of all the polarimetric constants relating to the sugars none have received the thorough study by numerous investigators that has been given to the specific rotation of sucrose. The formulæ of Tollens[36] and of Nasini and Villavecchia[37] giving the values at different concentrations, have been generally accepted as the most accurate. Landolt[38] has combined the two giving

$$\left[\alpha\right]^{20}_{\lambda=5892.5\,Å} = 66.435 + 0.00870\,\mathrm{C} - 0.000235\,C^2 \quad (C = 0 \text{ to } 65) \tag{29}$$

where C is the number of grams per 100 cc of solution.

Taking $C = 26.016$ we obtain from (29)

$$\left[\alpha\right]^{20}_{\lambda=5892.5\,Å} = 66^\circ502 \tag{30}$$

It will be observed that this value agrees fairly well with that given by (27), the difference being 0°027. However, the agreement is not as good as it should be. In view of the recent refinements in polarimetric measurement, we are of the opinion that 66°529 is very nearly correct and must be considered as more nearly representing the true value of the specific rotation than 66°502. It is interesting to note that the formula of Tollens gives the value 66°518.

The value 66°529 is obviously of about the same order of accuracy as the new conversion factor 34°620 given by (19), and the identical normal solutions were used in the determination of each. If the specific rotation be calculated from the Herzfeld-Schönrock conversion factor 34°657, the value obtained, when compared with 66°502 from (30), should give a direct check on the relative accuracy of the two conversion factors, 34°657 and 34°620. Our value of 99°89$_6$ S for the reading of the normal solution on the Herzfeld-Schönrock scale will thus be either proved or disproved.

---

[36] Ber., **10**, p. 1403 (1877).

[37] Public de lab. chim. delle gabelle Rome, p. 47 (1891).

[38] "Das optische Drehungsvermögen," p. 420 (1898).

Schönrock[39] has calculated the specific rotation by using 34°657. Taking that value and his saccharimeter reading, 100°03 S, for the normal solution, for $\lambda = 5892.5$ Å, he finds the rotation of the normal solution to be 34°667. By using the same method as that indicated for (27), he obtains 66°627 for the specific rotation; and calls attention to the fact that it is about 0°13 too large. This error is of such magnitude that even with no additional experimental data such as has been given in the present paper, it is evident that the value of 34°657 for the conversion factor, is too high. His value of 66°627 for the specific rotation is of course dependent not only on 34°657, but also on 100°03 S, and it is possible that the latter is in error, as is indicated by our corresponding value 99°99 S. In order to eliminate this possibility, we have calculated the specific rotation, using 34°620 and 100°03, and find 66°555 for the specific rotation. The agreement between 66°555 and the accepted value, 66°502, is much better than 66°627 and 66°502. The discrepancy must be attributed for the greater part to the fact that the Herzfeld-Schönrock conversion factor is too large. We therefore consider that the value 99°89$_6$ S for the reading of the normal solution on the Herzfeld-Schönrock scale is corroborated; and conclude that the available auxiliary data establishes the accuracy of the value 34°620, for the conversion factor, within reasonable limits.

We desire to take this opportunity to acknowledge our indebtedness to F. P. Phelps, who assisted in making computations and observations, and to C. F. Snyder, who performed many of the crystallizations.

---

[39] Zs. Ver. Zuckerind., 54, p. 553 (1904).

V. SUMMARY

1. Sucrose has been purified by concentrating aqueous solutions in vacuum below 35° C and crystallizing while in motion. For this work new apparatus has been devised.

2. It has been shown that reducing sugars are eliminated from the crystals by the above method. While no sample was found which failed to give a precipitate of cuprous oxide, it has been shown by the use of copper solutions of varying composition, and by a study of the reaction velocities of sucrose and of invert sugar, that sucrose itself was the cause of the precipitation.

3. The velocities of caramel formation at various temperatures have been determined; and the permissible time of heating plotted as a function of temperature. These data have been applied to the drying operations.

4. It has been shown that moisture can be eliminated from finely divided sugar by heating in a vacuum to 50° C for a few hours. This conclusion has been verified by a series of experiments at high vacuum extending over a long period of time. The absence of moisture has been shown by two direct qualitative tests.

5. A quantity of sugar has been fractionally crystallized and the various factions found to be identical in properties.

6. The ratios of the rotations of quartz and sugar for $\lambda = 5461$ Å and $\lambda = 5892.5$ Å have been determined. For quartz

$$\frac{\phi_{\lambda=5892.5\text{ Å}}}{\phi_{\lambda=5461\text{ Å}}} = 0.85085;$$

and for sugar

$$\frac{\phi_{\lambda=5892.5\text{ Å}}}{\phi_{\lambda=5461\text{ Å}}} = 0.84922$$

7. The reading of the normal sugar solution on the Herzfeld-Schönrock scale has been shown to be $99\overset{\circ}{.}89_8$ S.

8. The absolute rotation of the normal sugar solution has been determined with the following results:

Normal sugar solution $= 100^\circ = 34\overset{\circ}{.}617$ ($\lambda = 5892.5$ Å) at 20° C
Normal sugar solution $= 100^\circ = 40\overset{\circ}{.}763$ ($\lambda = 5461$ Å) at 20° C

9. The conversion factor has been determined for two monochromatic sources with the following results:

Normal quartz plate = 100° S = 34°620 (λ = 5892.5 Å) at 20° C
2°8885 S = 1° (λ = 5892.5 Å)
Normal quartz plate = 100° S = 40°690 (λ = 5461 Å) at 20° C
2°4576 S = 1° (λ = 5461 Å)

10. The difference between the rotations of the normal quartz plate and the normal solution for λ = 5892.5 Å, has been found to be 0°003, and for λ = 5461 Å, 0°073. These values indicate that the rotary dispersion curves of plate and solution cross at about $\lambda = 0.585\mu$. The reading of the normal solution on the true saccharimeter scale with the source λ = 5892.5 Å, has been calculated to be 99°99 S.

11. The difference in rotation in sugar degrees, for the normal solution on the saccharimeter, for the sources λ = 5461 Å and λ = 5892.5 Å, has been calculated from the absolute rotations, with the following result:

Saccharimeter reading$_{(\lambda=5461\ \text{Å})}$ − Saccharimeter reading$_{(\lambda=5892.5\ \text{Å})}$ = 0°19$_2$ S.

An independent experimental determination has been made of this difference and the value 0°18$_6$ obtained.

12. The thickness of the normal quartz plate has been calculated and the values 1.5934 mm and 1.5940 mm obtained.

13. The specific rotations of sugar for the normal solution for λ = 5892.5 Å and λ = 5461 Å have been calculated from the absolute rotations with the following results:

$$\left[\alpha\right]^{20}_{\lambda=5892.5\ \text{Å}} = 66^\circ 529$$

$$\left[\alpha\right]^{20}_{\lambda=5461\ \text{Å}} = 78^\circ 342$$

14. The agreement between the accepted value, 66°502, for the specific rotation and 66°529, in contrast to the disagreement between 66°502 and the specific rotation 66°627 from the Herzfeld-Schönrock conversion factor, has been shown to corroborate the new value, 34°620 (λ = 5892.5 Å), for the conversion factor.

WASHINGTON, September 30, 1915.

EFFECT OF IMPERFECT DIELECTRICS IN THE FIELD OF A RADIOTELEGRAPHIC ANTENNA

By John M. Miller, Assistant Physicist

Measurements by Fischer [1] and Austin [2] have shown that the curve which represents the variation of the resistance of an antenna with the wave length of the oscillation has two characteristic features. Starting from the wave length corresponding to the fundamental of the antenna, the equivalent resistance of the antenna rapidly decreases with increasing wave length, and reaches a minimum. As the wave length is still further increased, the resistance rises again, but in a linear manner (Fig. 2, *B*). The decrease in resistance is explained by a decrease in the energy radiated in the form of electromagnetic waves as the wave length increases. This so-called radiation resistance varies, as it should, inversely as the square of the wave length. It has been difficult, however, to account for the linear increase which takes place at the longer wave lengths, and it is with the explanation of this feature that the present paper is concerned.

A recent paper by Austin [3] pointed out the similarity in the linear increase in resistance of an antenna at long wave lengths with the behavior of an absorbing condenser. He noticed that the resistance curve obtained for an antenna was similar to that representing the equivalent series resistance of a glass condenser [4] and hence concluded that dielectric absorption was a probable explanation of the phenomenon. The fact that in the curves which he had obtained for ship stations the rise in resistance was less marked than for land stations led him to believe that the absorption was probably caused by the ground acting as an imperfect dielectric. Further confirmation of this view was apparently afforded by the curve for the high-power station at Arlington, Va. This station has a very good earth connection consisting of an extensive metallic earth net just below the surface of the ground. The resistance curve for this antenna, with the steel towers earthed, showed only a slight increase in resistance for the longer waves. Austin stated that if we consider the ground as a dielectric rather than a conductor and consider it as a portion of the total dielectric lying between the antenna regarded as the upper plate of a condenser, and the ground water regarded as the lower plate, we reach a very probable explanation of many antenna resistance curves. The measurements described in this paper verify Austin's hypothesis that the effect is caused by dielectric absorption, but do not confirm the supposition that the absorbing dielectric in question is the ground. Fig. 1 shows the values of the equivalent resistance ob-

---

[1] C. Fischer, Phys. Zs., **12**, p. 295; 1911.

[2] L. W. Austin, J. of Wash. Acad., **1**, p. 9, 1911; Phys. Zs., **12**, p. 924, 1911; this Bulletin, **9**, p. 65, 1912 (Scientific Paper No. 189); Jahrb. d. drahtl. Tel., **5**, p. 574; 1911–12.

[3] L. W. Austin, this Bulletin, **12**, p. 465, 1915 (Scientific Paper No. 257); Jahrb. d. drahtl. Tel., **9**, p. 498, 1915.

[4] In a perfect condenser, or one which shows no energy loss, the phase of the current (I) is 90° in advance of the electromotive force (E). In an imperfect condenser the power loss, however caused, is given by $IE \sin \theta$, where θ is the phase difference or the angle by which the current lags from quadrature. An equivalent power loss is occasioned by a resistance (ρ) in series with a perfect condenser when this equivalent resistance satisfies the relation $\tan \theta = Cp\rho$ where C is the capacity and $p = 2\pi$ times the frequency. It is characteristic of a condenser with an absorbing dielectric that the phase difference θ is, roughly, independent of the frequency, and hence the equivalent resistance must vary inversely as the frequency or directly as the wave length.

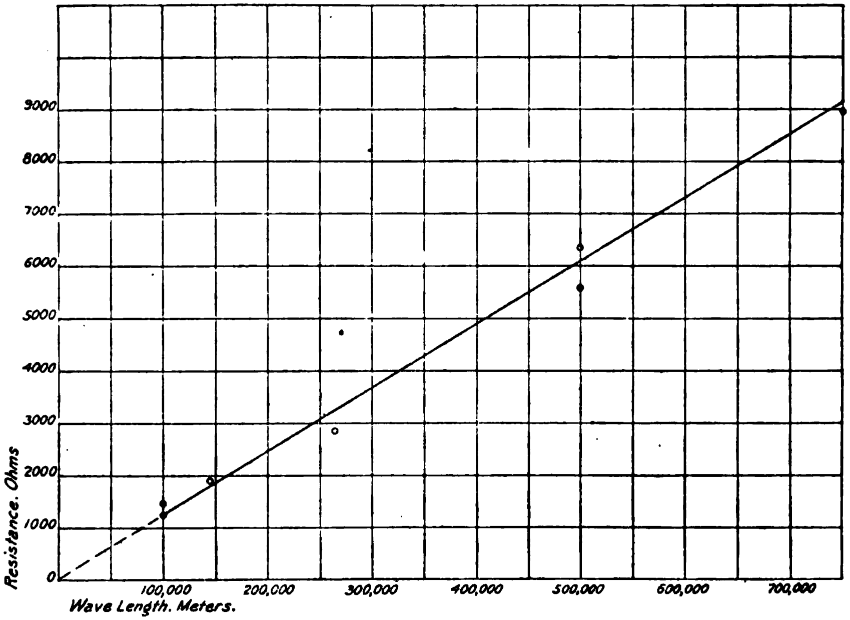


FIG. 1.—*Equivalent resistance of an antenna at telephone frequencies*

tained at telephone frequencies for a small flat top antenna at the Bureau of Standards. This antenna runs from a building to a tree and has a capacity of 650 micro-microfarads (0.00065 microfarad). The measurements were made at wave lengths varying from 100 000 to 750 000 meters, the equivalent resistance increasing linearly from 1000 to 9000 ohms. This is the order of magnitude which would be expected from Austin's measurements at wireless frequencies upon an antenna for which the rise in resistance was particularly marked.

It seemed impossible, however, to ascribe this absorption to the ground acting as an imperfect dielectric. The effect persisted at telephone frequencies while the calculations of True[5] and Reich,[6] based upon the measurements of conductivity and dielectric constant of the ground as given by Zenneck[7] show that even for so high a frequency as would correspond to a wave length of 1000 meters the magnitude of the conduction current in the ground exceeds by a hundred times that of the displacement current. The absence of absorption in the ground was also shown by measurements at telephone frequencies upon a guard plate condenser with part air and part clay between the plates. This condenser behaved as a perfect condenser with a series resistance that was independent of the frequency. Only when the clay was exceedingly dry and particularly when it was loosely packed was there any indication of absorption.

The observed large effect upon the absorption of variable air condensers brought about by the poor dielectric properties of small amounts of insulators in the electric field suggested to the author that the absorption in antennas is likewise caused by the presence of poor dielectrics in the field of the antenna. Accordingly, an experimental antenna was built in which the bad effects of poor dielectrics in the neighborhood were carefully avoided but in which any absorption that might be caused by the ground would be considerably magnified. The main capacity of the antenna consisted of six parallel wires at a distance of about 0.3 of a meter above the surface of the ground and located at a considerable distance from the nearest building or tree. The antenna was supported by four wooden posts, but was insulated from them by double porcelain insulators spaced about a meter apart. A single lead, similarly insulated, ran to the building in which the measurements were made. The earth connection was made to the water pipes of the building. The proximity of the antenna wires to the ground should reduce the lateral spread of the electrostatic field and hence the displacement through the wooden posts or other poor dielectrics, while the amount of ground between the antenna wires and ground water would be proportionately increased. The double-spaced insulators also served to reduce the capacity through the supports. The capacity of the antenna was 850 micro-microfarads.

---

[5] H. True, Jahrb. d. drahtl. Tel., **5**, p. 125; 1911-12.

[6] M. Reich, Jahrb. d. drahtl. Tel., **5**, pp. 176, 253; 1911-12.

[7] J. Zenneck, Ann. d. Phys., **23**, p. 859; 1907.

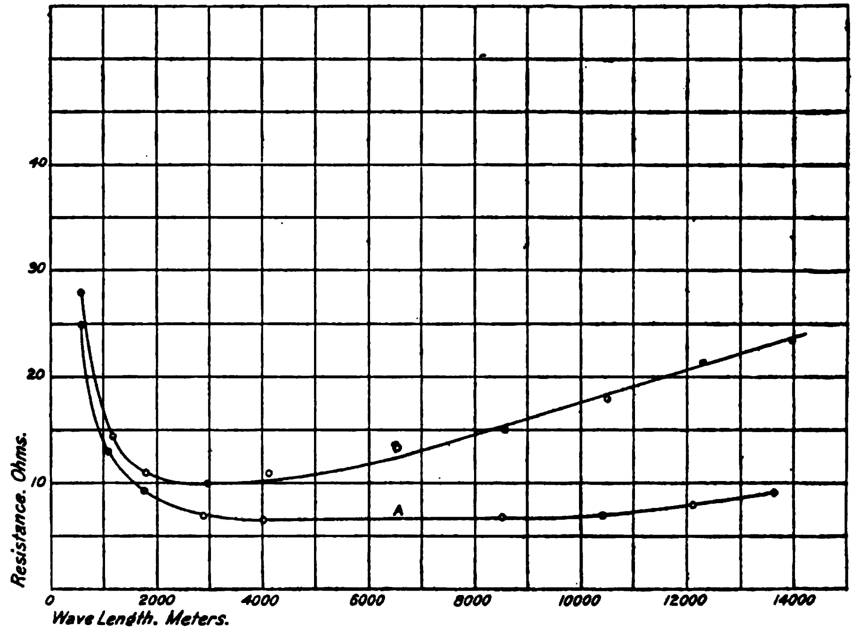


FIG. 2.—*A, Resistance curve for antenna with extremely small absorption; B, effect of adding small imperfect capacity through the wooden supports*

The resistance measurements were made by the "artificial antenna" method in which a small inductance and a condenser with a resistance in series are substituted for the antenna. The series resistance is so adjusted as to give the same current effect when the substitution is made. The resulting resistance curve, for measurements made just within the window of the building, is shown in curve *A* of Fig. 2. The rise in resistance even at 12 000 meters is very small and probably caused by the lead wire to the building. The result was also verified at telephone frequencies where the absorption was barely detectable (less than 60 ohms at 3000 cycles).

Curve *B* of the same figure shows the effect produced by adding a small capacity through the wooden supports. Wires were run from the insulated portion of the antenna to porcelain insulators on three of the stakes, the total capacity being increased by only 40 micro-microfarads or less than 5 per cent. The effect of adding this small imperfect condenser is very marked. The linear increase in resistance becomes pronounced, and *brings with it an increase in the resistance of the antenna at all wave lengths.* Austin's measurements upon ship stations were made upon battleships, where the antennas were supported from steel masts, and it is probable that this fact may explain the slight rise of the curves obtained for such stations.

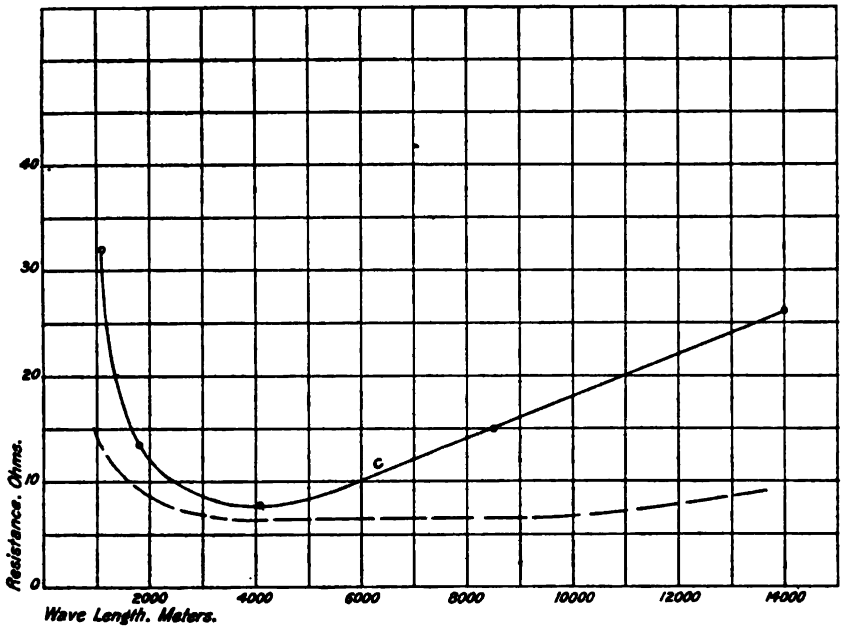


FIG. 3.—*C, Absorption effect produced by the portion of the leads to an antenna inside of a building*

The effect of running the lead wires to an antenna inside of a building was also investigated. Curve *C* of Fig. 3 shows the results upon the above described antenna under the same conditions as those obtaining for curve *A* of Fig. 2 (reproduced in dash lines in Fig. 3), excepting that the measurements were made within the room at a distance of about 5 meters from the window. The increase in capacity in this case was 60 micro-microfarads. Curves *D* and *E* of Fig. 4 were obtained for antennas completely within the building (using the same water-pipe ground as before), the former having a capacity of 290 micro-microfarads, the latter having double the capacity. In this figure the scale of resistances has been doubled. It is of interest to note that the equivalent series resistance in the case of the smaller capacity

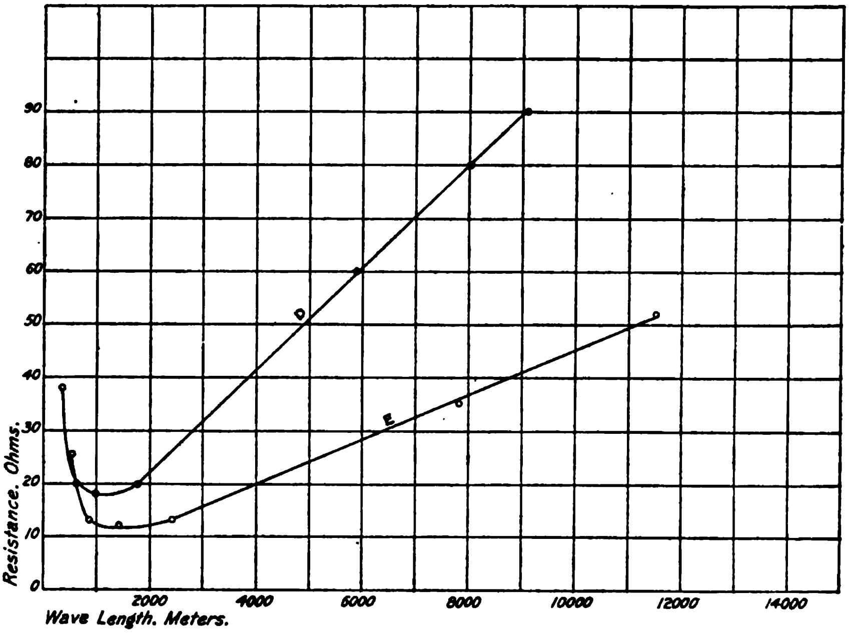


FIG. 4.—*Resistance curves for antennas completely within a building. The capacity for E is twice that for D*

is approximately double that for the capacity of twice the size, which is the requisite condition for absorbing condensers with the same phase difference. Measurements, at telephone frequencies, were also made upon an antenna consisting of three wires stretched vertically along the outside of a brick building at a distance of 0.4 of a meter from the wall. The phase difference of the condenser was about 15 minutes, corresponding to an equivalent resistance of about 25 ohms at 10 000 meters for a capacity of 800 micro-microfarads. The phase difference is about the same as that obtained in the case of antennas within the building.

Finally the effect of a tree upon the absorption of an antenna was investigated. An antenna consisting of two parallel wires was strung from a building to a tree 20 meters distant at an average height of about 5 meters from the ground. The antenna terminated in a section of about 6 meters of wire which ran from limb to limb of the tree, but was insulated from it by porcelain insulators. At a distance of about 2 meters from the tree double porcelain insulators were interposed in each antenna wire, so that measurements could be made with the section in the tree included or excluded (using the same water-pipe ground as before). Curve *F* of Fig. 5 was obtained for the latter case, while curve *G* shows the enormous absorption produced by including the portion of the antenna in the tree. The capacity was increased from 390 to 540 micro-microfarads, and the phase difference of the condenser with the portion in the tree included was roughly 2°. The measurements were made this winter when the tree was free from foliage.

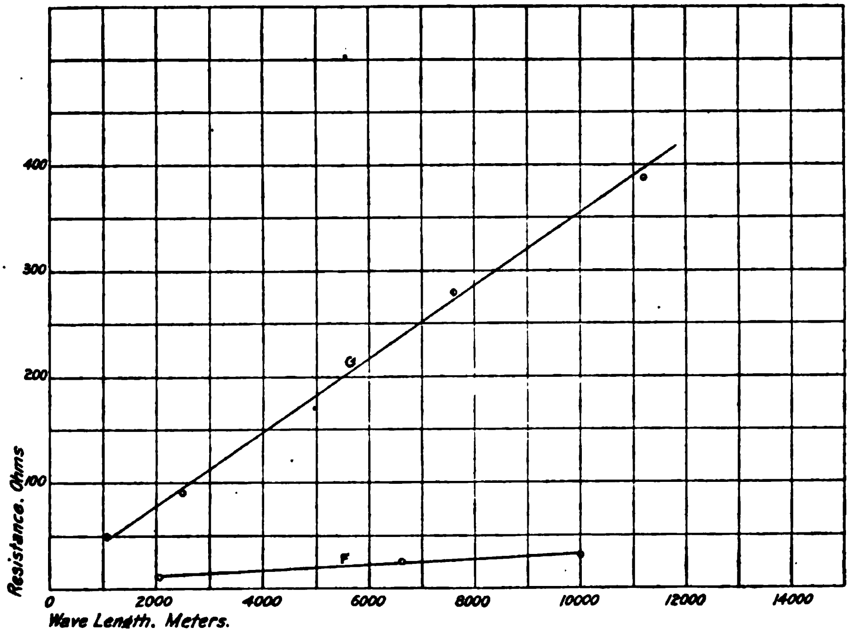


FIG. 5.—*Curve G shows the enormous absorption caused by a tree. Curve F is the same antenna with portion in tree excluded*

From the above it is evident that in the design of an antenna it is a matter of importance to keep the dielectric absorption of the antenna, regarded as a condenser, as low as possible in order to minimize the waste of energy in the antenna and so improve its efficiency as a radiator. There is a possibility of greatly improving upon the design of existing antennas in this respect. The requirement is that the capacity through wooden masts, trees, buildings, insulators, etc., must be made extremely small in comparison to the capacity of the antenna through unobstructed air. In other words, the electrostatic field of force set up by the oscillating electric charges should not be occupied by imperfect dielectrics, and especially so where the electric force is intense. One important feature of design is to cover the interior walls of rooms into which the leads to the antenna run with grounded metal screens.

SUMMARY

The characteristic linear increase in resistance of radiotelegraphic antennas with increasing wave length (which predominates at the longer wave lengths over the decrease due to decreased radiation) is shown to be caused by dielectric absorption in imperfect dielectrics in the electric field of the antenna, as suggested by Austin.

It is shown, however, by measurements both at wireless and telephone frequencies that the absorption does not take place in the ground, but in poor dielectrics such as wooden masts, trees, buildings, insulation with poor dielectric properties, etc., in the field of the antenna, the effect being also produced when the leads to an antenna are brought within a building.

The practical importance of considering this dielectric absorption in the design of antennas is pointed out in order to increase the efficiency of the antenna as a radiator of electric energy.

In conclusion, the author desires to express his indebtedness to M. James, of this Bureau, who first suggested and carried out absorption measurements upon an antenna at telephone frequencies, and to Dr. Rosa, who was in charge of this investigation, for his many valuable suggestions during the course of the work.

WASHINGTON, January 7, 1916.

LUMINOSITY OF A BLACK BODY AND TEMPERATURE

By Paul D. Foote and C. O. Fairchild

The relation between luminosity and temperature has been studied quite extensively by many investigators, especially Dr. Ives and Dr. Nutting. Recently an interest has arisen in the subject from the standpoint of pyrometry. With the relation between luminosity and temperature established, a pyrometer may be devised for the measurement of temperature by means of observations upon the luminosity of a source, more especially a black body.

Two equations have been deduced representing this relation, one by Rasch and the other by Nutting. In the present paper these equations are derived by a new method, and a new equation also is obtained, which, however, is not essentially different from that derived by Nutting.

Luminosity is defined as the integral from *o* to ∞ in respect to $d\lambda$ of the product visibility, V, and energy, J, of the radiating source thus

$$L=\int^{\infty} VJd\lambda \tag{1}$$

where

$$V=f(\lambda)$$

$$J=c_1\lambda^{-5}e^{-c_2/\lambda\theta}=\text{Wien's law.}$$

The effective wave length, λ_L, of the luminosity has been defined analytically by one of the writers[1] in the following manner:

$$\lambda_L=\frac{\int_0^{\infty} VJd\lambda}{\int_0^{\infty}\frac{VJ}{\lambda}d\lambda} \tag{2}$$

The physical significance of this so-called effective wave length as far as optical pyrometry is concerned has been discussed elsewhere. But regarding equation (2) for the time being as simply a numerical relationship, the following expression is true:

---

[1] Foote, J., Wash. Acad. Sci., 5, p. 526; 1915. Complete paper, this Bulletin, 12, p. 483, 1916. See also Hyde, Cady, and Forsythe, Phys. Rev., 6, p. 70, 1915; Astrophys. J., 42, pp. 294-304; 1915.

$$(3)\qquad \frac{d\log L}{d\theta}=\frac{c_2}{\theta^2}\cdot\frac{\int_0^\infty \frac{VJ}{\lambda}d\lambda}{\int_0^\infty VJd\lambda}=\frac{c_2}{\theta^2}\,\frac{1}{\lambda_L}$$

Suppose that equation (2) is of the form:

$$(4)\qquad \lambda_L=a+b/\theta+c/\theta^2+\ .\ .\ .\ .\ .$$

where a, b, c, etc., are dimensional constants.

Accordingly, if λ_L is expressed as a known function of θ, this function may be substituted in (3), integrated, and $L=f(\theta)$ obtained.

The quantity λ_L is the value of the λ – coordinate of the center of gravity of the curve $\frac{JV}{\lambda}$ versus λ, not of the luminosity curve, as sometimes assumed. In the present work values of λ_L for temperatures ranging from 1000 to 7000° absolute were obtained directly from the $\frac{JV}{\lambda}$ versus λ curves by means of the Amsler Integrator No. 1; the values of J for various wave lengths were computed from Wien's law, using $c_2=14450$ micron degrees,[2] and the values of $V=f(\lambda)$ were obtained as a mean of data by Ives,[3] Nutting,[4] and Hyde and Forsythe.[5] No experimental observations are included in the present paper, the primary object of which has been to point out a simple method of deriving the luminosity-temperature relations and to consider their applicability to temperature measurement.

The possible forms of the luminosity equation are as follows:

Case I, $\lambda_L=a$, i. e., the constants b, c, etc., of equation (4) are zero.

Substituting in (3) and integrating:

$$(5)\qquad \log L=-\frac{c_2}{\lambda_L}\cdot\frac{1}{\theta}+\text{const.}$$

This is the well-known Rasch[6] equation which has been recently applied by Langmuir[7] for the determination of the melting point of tungsten. The value of $\lambda_L=a$ is known as the Crova wave length because Crova[8] first pointed out that there exists a wave length in the spectral energy curves of two sources at which the ratio of the radiation intensities equals the ratio of their total luminosities. This wave length has generally been considered to be $\lambda_L = a = 0.58\mu$. Ives [9] and Pirani [10] showed, however, that the value is not constant if the radiation from black bodies at various temperatures is compared, the wave length shifting slightly toward the green as the temperatures of the sources increase. Equation (5) may be written as follows:

---

[2] Coblentz, this Bulletin, **10**, pp. 1–77; 1914.

[3] Ives, Phil. Mag., December; 1912.

[4] Nutting, Phil. Mag., **29**, p. 306; 1915.

[5] Hyde and Forsythe, Phys. Rev., **6**, p. 70; 1915.

[6] Rasch, Ann. Phys., **14**, p. 193; 1904.

[7] Langmuir, Phys. Rev. (2), **6**, p. 138; 1915.

[8] Crova, Compt. rend., **98**, p. 512; 1881.

$$L = Ae^{-c_2/\lambda_L\theta} \tag{6}$$

Case II, $\lambda_L = a + b/\theta$

Substituting in (3) and integrating:

$$L = A\left(\frac{B}{\theta} + 1\right)^{-C} \text{ where } B = \frac{b}{a} \text{ and } C = \frac{c_2}{b}. \tag{7}$$

This is the equation derived by Nutting [11] by obtaining a mathematical expression for $V = f\ (\theta)$ and substituting in equation (1) and integrating.

Case III, $\lambda_L = a + b/\theta + c/\theta^2$

whence from equation (3)

$$L = A\left(\frac{B+\theta}{C+\theta}\right)^D \text{ where} \tag{8}$$

$$B = \frac{b - \sqrt{b^2 - 4\,ac}}{2\,a}$$

$$C = \frac{b + \sqrt{b^2 - 4\,ac}}{2\,a}$$

$$D = \frac{c_2}{\sqrt{b^2 - 4\,ac}}$$

Case III, and in general Case II, are sufficiently accurate for representing the luminosity of a black body at various temperatures from 1000 to 7000° absolute. Table 1 and Fig. 1 show the variation of λ_L with θ. For comparison, the values of the wave length corresponding to the centers of gravity of the luminosity curves are also shown. The difference between these wave lengths, λ_{cg}, and the true "effective" wave lengths is slight—about 0.003μ.

---

[9] Ives, Phys. Rev., 32, p. 316; 1911. See also Ives and Kingsbury, Washington meeting of Ill. Eng. Soc.; 1915.

[10] Pirani, Verh. d. Phys. Ges., p. 219; 1915.

[11] Nutting, this Bulletin, 5, p. 306; 1915. Also Phil. Mag., 29, p. 306; 1915.

TABLE 1

Temperature, degrees absolute	λ_L (μ)	λ_{cg}	Luminosity, relative units	Rasch "A" at 3000°	Per cent dev. $\frac{\text{True-Rasch}}{\text{True}}$	Nutting	Per cent dev.	Case III	Per cent dev.
1000	0.6100	0.6125	0.4936×10^{-6}	0.2542×10^{-6}	+48.0	0.4750×10^{-6}	+3.8	0.4891×10^{-6}	+0.91
1500	.5898	.5923	$.1505\times10^{-3}$	$.1257\times10^{-3}$	+16.0	$.1475\times10^{-3}$	+2.0	$.1497\times10^{-3}$	+ .53
2000	.5784	.5810	.09255	.08839	+ 4.5	.09192	+ .68	.09243	+ .13
2500	.5710	.5740	1.143	1.134	+ .79	1.142	+ .09	1.142	+ .088
3000	.5661	.5692	6.209	6.209	0.00	6.241	− .52	6.214	− .080
3500	.5625	.5654	21.02	20.93	+ .42	21.07	− .24	21.04	− .095
4000	.5599	.5629	52.60	52.09	+ .97	52.92	− .61	52.75	− .28
4500	.5575	.5603	108.0	105.8	+ 2.0	108.8	− .74	108.2	− .18
5000	.5557	.5589	192.25	186.6	+ 2.9	193.7	− .75	192.7	− .23
5500	.5543	.5574	309.1	296.8	+ 4.0	310.7	− .52	309.4	− .10
6000	.5531	.5560	459.1	436.6	+ 4.9	461.7	− .57	459.5	− .09
6500	.5520	.5551	640.9	605.5	+ 5.5	644.8	− .61	642.6	− .26
7000	.5511	.5541	854.6	801.9	+ 6.2	858.5	− .46	856.9	− .27

Average deviations: Rasch, 7.4 per cent; Nutting, 0.89 per cent; "Case III," 0.25 per cent.

Using the data for λ_L in Table 1, the following are the luminosity equations:

Case I. $\lambda_L = a =$ mean of all values of $\lambda_L = 0.5663$

$$L = 30700e^{\frac{-25517}{\theta}} \text{ (relative units)}$$

Case II. $\lambda_L = .5421 + \frac{69.732}{\theta}$ (least square solution)

$$L = 37400\left(\frac{128.63}{\theta} + 1\right)^{-207.22} \text{ (relative units)}$$

Case III. $\lambda_L = .53915 + \frac{86.017}{\theta} - \frac{15160}{\theta^2}$ (least square solution)

$$L = 37790\left(\frac{\theta - 105.92}{\theta + 265.46}\right)^{72.1662} \text{ (relative units)}$$

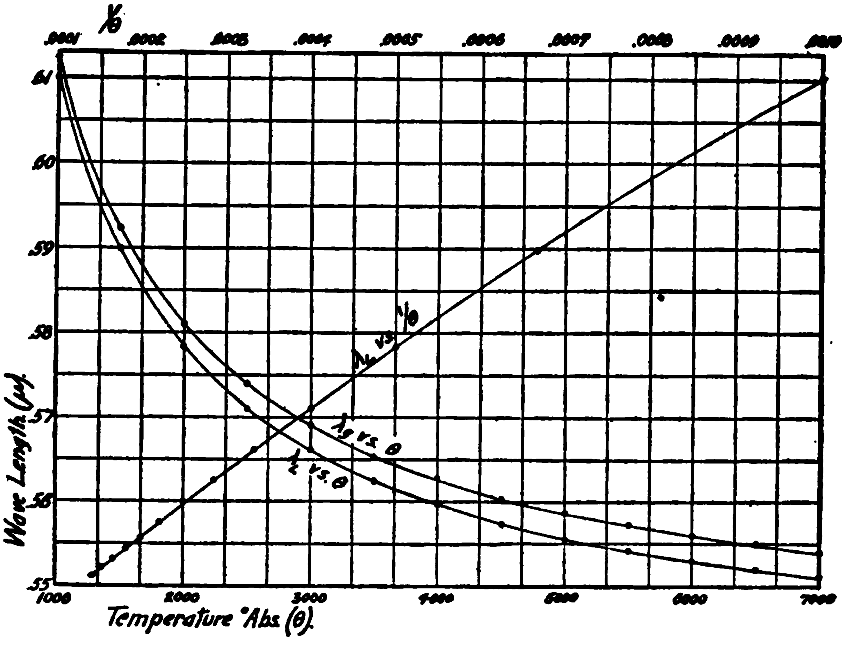


FIG. 1.—*Effective wave length and "center of gravity" as a function of the temperature*

Table 1 contains the computations of luminosities by these three equations. The equation represented by Case III fits the luminosity-temperature curve (computed on the basis of Ives', Nutting's, and Hyde and Forsythe's visibility data) with no deviations larger than the errors involved in the determination of L by the planimeter. The Nutting equation holds almost as accurately, but the Rasch equation is entirely unsatisfactory. In the table the Rasch equation has been arbitrarily made to agree with the observed luminosity at 3000° absolute, since the mean value of the Crova wave length from 1000 to 7000° is the Crova wave length at this temperature. When thus adjusted the equation is in error by nearly 50 per cent at 1000° absolute.

Application of the above equations to the measurement of temperature:

Either the Nutting formula or the equation represented by Case III is applicable to temperature measurement of a black body. The Rasch formula should not be used. As an example of the errors, expressed in temperature, which may be expected from the use of this latter equation, suppose the luminosity pyrometer were calibrated at 3000° absolute:

True θ	Observed θ	Error, degrees
1000	1027	27
3000	3000	0
7000	7125	125

If the pyrometer were calibrated at about 1000° absolute, then:

True θ	Observed θ	Error, degrees
1000	1000	0
3000	3227	227
7000	9800	2800

Data on the luminosity-temperature relation of a black body are so meager and unsatisfactory that as yet it does not appear advisable to assign absolute values to the constants A in formulas 7 and 8. A cursory summary of experimental determinations by various observers is given in Table 2. Many of these data are old and based on incorrect temperature scales. Expressing the luminosity in candles/cm^2 they give a numerical value of A in equation (8), Case III, as follows:

$$A = 2.0 \times 10^7.$$

TABLE 2

Temperature, degrees absolute	Candles/cm^2	Authority	$A/10^7$, Case III
1449	0.38	Lummer and Pringsheim	1.70
1597	2.0	do	1.87
1707	5.8	do	2.00
2028	82.	Nernst	2.82
1462	0.34	do	1.31
1596	2.17	do	2.05
1693	4.8	do	1.87
2623	1089.	do	2.24
2027	59.	do	2.04
2182	162.	do	2.33
2290	245.	do	2.05
2013	47.	do	1.77
2077	73.	do	1.88
2097	90.	do	2.06
2101	100.	do	2.25
2101	101.	do	2.26
2104	79.	do	1.74
2107	86.	do	1.88
2245	202.	do	2.10
2284	225.	do	1.93
1947	40.	Pirani	2.30
2150	127.	do	2.17
Mean A=			2.0×10^7

Langmuir[12] applied the Rasch equation, with constants determined by Nernst, for the determination of the melting point of tungsten. This immediately raises the question cited by Langmuir as to whether any luminosity equation derived for a black body is applicable to nonblack bodies. If the nonblack body is gray and if the emissivity is constant with temperature, the equations are directly applicable either for obtaining the apparent blackbody temperature or, after correcting the luminosity by $1/E$ where E = emissivity coefficient, they are applicable for obtaining the true temperature. The best data upon this question appear in a recent paper by Paterson and Dudding,[13] who conclude that for all practical purposes many nonblack materials are gray. Their observations upon the melting point of platinum by color match with a black body confirm this conclusion. However, if nonblack materials are not gray to all practical purposes and if metals do possess a temperature coefficient of emissivity in the visible spectrum, it would still be possible to represent the luminosity by an equation of the form of equation (8), although the constants would differ from those obtained for a black body. Making Langmuir's assumption that the luminosity equation for a black body is directly applicable to tungsten, and that the observed luminosity, 6994 candles/cm^2, can be corrected to correspond with a black body by the factor $1/E = 1/.51$ and using, instead of the Rasch equation, the equation given under Case III, where $A = 2.0 \times 10^7$, the melting point of tungsten would be 3602° absolute. In Langmuir's[14] paper, page 139, is given the Rasch equation with the constants determined by Nernst, when the temperature is based on the melting point of gold = 1064° C. If the equation there cited is supposed to hold at this temperature and this supposition is warranted from Nernst's paper,[15] the luminosity at the melting point of gold is .08361 candles/cm^2. Taking the correct temperature at the melting point of gold as 1063° C the constant A of equation (8) becomes $1.553 \cdot 10^7$. This leads on the basis of Langmuir's data to a value of $\theta = 3734°$ absolute for the melting point of tungsten. The value obtained by Langmuir is 3528° absolute. It is more than likely that the value 3528 is nearer correct than 3734, but three things must be done before any value obtained by a luminosity method is accepted: (1) The Rasch equation must be discarded; (2) the luminosity of a black body at a known temperature must be determined accurately; and (3) further proof is required that the constants determined in the luminosity-temperature relation for a black body apply even approximately for a nonblack body.

---

[12] Langmuir, Phys. Rev. (2), 6, p. 138; 1915.

[13] Paterson and Dudding, Proc. Phys. Soc. Lond., 27, p. 230; 1915. Also Phil. Mag.; 1915.

Note on the maximum luminous efficiency of a black body: The highest luminous efficiency which a black body can possess occurs at a temperature such that:

$$\frac{\int_0^\infty VJd\lambda}{\int_0^\infty Jd\lambda} = \frac{L}{\text{const.} \times \theta^4} = \text{maximum.}$$

Substituting L from equation (8) and evaluating one obtains $\theta_{\text{max}} = 6547°$ absolute. Another means for obtaining θ_{max} is by evaluating the terms on the left of the above equation. The following relation is then obtained:

$$4\lambda_L\theta_{\text{max}} = c_2$$

If one plots the product 4 × effective wave length × absolute temperature versus θ, the value of θ corresponding to $4\lambda_L\theta = c_2$

---

[14] Loc. cit.

[15] Phys. Zs., 7, p. 382; 1906.

is the temperature of the highest luminous efficiency whatever be the luminosity-temperature relation.

SUMMARY

The relation between luminosity of a black body and temperature has been derived by a new method. The Rasch equation is shown to be unsatisfactory, while the Nutting equation or a slight modification of the Nutting equation holds exceedingly well. The exact meaning of the Crova wave length is defined by equation (2) and is shown to be of the form $\lambda_L = a + b/\theta + c/\theta^2$.

The luminosity pyrometer appears advantageous for temperature measurements when calibrated in terms of the Nutting equation or the suggested modification of Nutting's equation. Precise measurements on the luminosity-temperature relation of a black body are greatly to be desired.

WASHINGTON, November 18, 1915.

INCLUSIONS IN THE SILVER VOLTAMETER DEPOSITS

By G. W. Vinal and William M. Bovard

CONTENTS

Page
1. Introduction 147
2. Apparatus employed 149
    The electric furnace 149
    For heating by the flame method 150
    The silver voltameters 151
3. The alloying of silver and platinum 152
4. Effect of alloying on the amount of silver deposited 157
5. Estimation of inclusions in deposits from pure electrolytes 159
6. The value of the Faraday 162
7. Additional experiments on the deposits 163
    Successive heatings of the deposits 163
    Effect of heating deposits to an abnormally high temperature 163
    Effect of prolonged heating of the deposit 164
    Heating the deposit after removal from cathode 164
    The inclusions between the crystals and the surface of the cup 165
    Inclusions in silver deposits from less pure electrolyte 167
    The volume effect 167
8. Experiments on the anode liquid 169
9. Summary 171

1. INTRODUCTION

In a previous paper[1] in this Bulletin a brief discussion of the question of inclusions of foreign materials in the silver voltameter deposits was given, together with a short résumé of other papers on this subject and a few experiments which had been made at the Bureau of Standards. It was pointed out that in so far as the international ampere is concerned the value assigned to the electrochemical equivalent of silver by the London conference has been generally accepted by the various national laboratories as applying to the silver as we find it deposited in the voltameter without reference to any inclusions that it may contain. This is not a serious matter, because the uniformity of the results obtained by the national laboratories working together indicated that the inclusions must be very small or very constant in amount, and the international committee was enabled to fix the voltage for the Weston normal cell with sufficient accuracy for present purposes. But it was also stated in the reference mentioned above that it is important, if possible, to eliminate any error due to the inclusions in order that we may know what deviation there is, if any, from the value assigned to the electrochemical equivalent of silver (1.11800 mg per coulomb).

---

[1] The Silver Voltameter, Part IV, by Rosa, Vinal, and McDaniel. This Bulletin, 10, p. 516, Reprint No. 220.

The earliest experiments of the Bureau on the inclusions in the silver were few in number and were not considered conclusive. Only one deposit was heated to incandescence, and that was from an electrolyte in which impurities were purposely introduced. Its result had, therefore, no significance so far as the value derived for the Weston normal cell was concerned, since only pure electrolytes were used for that purpose.

We have now carried out at the Bureau some further experiments, principally to determine the loss of weight of the deposits when heating them to temperatures of 600° or more. These will be recorded in the present paper, and also a few experiments bearing on the question of the anode liquid.

Richards and Anderegg[2] have recently made determinations of the inclusions of foreign material in the silver deposits. They found the inclusions in their deposits to be very variable and large enough to be a serious source of error in the silver voltameter determinations. They recommended as a safe and convenient method for determining these inclusions that the platinum cups containing deposits should be heated to dull redness in a flame and reweighed.[3] The resulting loss in weight they attributed to the expulsion of foreign material in the deposit. We have repeated this part of their work, and we have extended the experiments to include comparisons with the effect when similar deposits are heated in an electric furnace. Van Dijk[4] has previously used a furnace for this purpose. Our furnace was considerably larger than his, so that we could heat our regular platinum cathodes in it.

---

[2] J. Am. Chem. Soc., 37, p. 15; 1915.

[3] Essentially the same method has been previously described and used by Lord Rayleigh and Mrs. Sedgwick, Phil. Trans., 175, p. 430, 1884; Jaeger and von Steinwehr, Zs. f. Instrk, 28, p. 354, 1908; Boltzmann, Sitzber. Akad. Wiss., Wien, IIA, 121, p. 1060, 1912.

[4] Ann. d. Phys., 19, p. 263; 1906.

We found the losses on glowing the deposits to be only 0.004 per cent on the average and fairly constant. We also found that both these methods of heating the deposits are subject to a source of error. In order to drive the inclusions out of the deposited silver a temperature of about 600° has been used, and there is necessarily more or less alloying of the silver with the platinum cup. On removing this silver there is left behind a stain of platinum black. This may be so slight as to be hardly noticeable, but if deposits are made without entirely removing the stains the deposited silver does not accurately represent the quantity of electricity that has passed through the voltameter, and if such a deposit is heated to dull redness the observed loss in weight depends more on the loss of adsorbed material from the platinum black than on the expulsion of inclusions from the deposited silver. This source of error was not mentioned by previous observers.

2. APPARATUS EMPLOYED

The electric furnace was designed and built by Prof. G. A. Hulett for this work and we are greatly indebted to him for the use of it. It was constructed from a glazed porcelain beaker and the heating coils of nichrome wire were wound not only on the sides and bottom but there was also a heating coil in the porcelain cover in order to provide as uniform a temperature inside as possible. Temperature measurements were always made by a platinum platinum-rhodium thermocouple which had been calibrated at this Bureau. The thermocouple passed into the furnace through a porcelain tube in the center of the cover. The outside of the furnace consisted of two concentric hollow cylinders of metal and asbestos. The double air space thus provided gave ample heat insulation to make the furnace efficient for temperatures not exceeding 750° C. The top of the furnace was of glazed porcelain rings, one of which supported the interior parts. The outside dimensions of the furnace are 21 cm diameter by 27 cm high and the inside dimensions are 9 cm diameter by 16 cm.

The platinum cups, one at a time, were lowered into the furnace with platinum-tipped tongs and rested on a network of platinum wires woven in a perforated porcelain plate. The cups were covered with glazed porcelain crucible covers to prevent the accidental falling of any particles into them when putting the thermocouple in place. The electric current was applied gradually by steps of 1 ampere at intervals of a few minutes until the maximum current of 7.7 amperes was reached. After each heating the furnace was allowed to cool to about 300° before opening it.

The furnace was designed with a view of avoiding the difficulties of metal contamination sometimes encountered with platinum-wound furnaces.[5] To test this an empty platinum cup was heated four times and weighed after each heating with the results given in Table 1.

TABLE 1

Date	Weight of cup	Δ	Treatment of cups
1915	g	mg	
July 23	38.496887	−0.024	Washed and dried at 160°.
	942	+ .031	Heated to 650°.
	897	− .014	Heated to 648°.
July 24	897	− .014	Heated to 646°.
July 26	932	+ .021	Heated to 648°.
Mean	38.496911	± .021	

Each of the five determinations given in Table 1 is subject to the same experimental error in so far as the weighings are concerned. Since the deviations are by small amounts, the results show that the heating to a high temperature was without effect on the weight of the cup.

For heating by the flame method the platinum cups were supported on a quartz triangle and covered with a small glazed porcelain evaporating dish. The room was darkened and the cup heated quickly and as uniformly as possible to a very dull red with a Bunsen burner held in the hand. We made a number of determinations on empty platinum cups to determine the effect of heating. The following results, Table 2, give the weight after each heating to about 600° C:

---

[5] Proc. Am. Acad. Sci., 38, p. 460; 1903.

TABLE 2

Date	Weight of large cups	Δ	Weight of small cups	Δ	Treatment of cups
1915	g	mg	g	mg	
June 10	80.293412	+0.004	38.495585	+0.003	Washed, dried, and glowed.
	404	−.004	579	−.003	Heated to dull redness.
Mean	80.293408	±.004	38.495582	±.003	
June 11	80.293183	+.068	38.494855	+.047	Washed and dried at 160°.
	113	−.002	805	−.003	Heated to dull redness.
	082	−.033	788	−.020	Do.
June 12	083	−.032	786	−.022	Do.
Mean	80.293115	±.034	38.494808	±.023	
Average Δ's of both sets		±.024		±.017	

The results of Table 2 show very little change, if any, in the weight of the empty cup due to heating them to redness. In all the succeeding work the empty cups were glowed each time before weighing them.

When heating the cups with silver deposits to dull redness, the porcelain dish serving as a cover for the cup was examined for any traces of volatilized silver, but none was ever seen nor was any found by chemical tests. During the heating process the observer listened for the "series of small explosions" mentioned by Richards and Anderegg,[6] but this phenomenon was never observed.

The silver voltameters were the same instruments as used in the previous work at the Bureau of Standards together with the voltameters previously used in the Princeton laboratory. To these were added two silver cups identical in size and shape with the Princeton platinum cups. It has generally been thought impossible in the past to use silver cups, partly because the deposit can not readily be removed and the cup restored to its original condition and partly because of inconstancy of weight when heated. Both of these objections were mentioned by Lord Rayleigh.[7] Recently it has been found in the work at Princeton that silver deposited on *highly polished silver* may be scraped off with the greatest ease, although it adheres sufficiently well for the usual washing operations. The deposit, after being washed, was scraped down, while still wet, with a small silver "hoe." This has afforded a ready means of determining the inclusions between the crystals and the cup and of saving deposits for further examination for inclusions. Prof. Hulett has kindly permitted us to make use of his silver cups in this way.

---

[6] Loc. cit., p. 9.

[7] Phil. Trans., 175, p. 431; 1884.

The electrolytes used in these experiments were generally of a very high degree of purity and the silver nitrate was prepared either by the methods [8] previously described by the Bureau or by the Princeton method. The electrolyte was always tested for its acidity and for reducing agents.

The cups were weighed on the same balances described by Rosa and Vinal,[9] but these balances were mounted in a new balance room, similar, however, to that used before.

3. THE ALLOYING OF SILVER AND PLATINUM

Nearly all the previous observers who have tried heating the silver deposits have mentioned the alloying of the silver and platinum at a temperature corresponding to dull red, and Van Dijk [10] has described the black stain left on the platinum cup after the silver has been removed. Others have not mentioned this, probably because the stain was almost invisible if the alloying was slight. None of the previous authors seem to have been aware of the significance of this alloying and of the black stain; for example, Richards and Anderegg [11] say, "Such heating slightly alloys the two metals * * *. This complication, of course, has not the slightest effect upon the quantitative experiment."

Time, as well as temperature, is a very important factor in alloying. Rapid heating to a given temperature for a short time may produce little effect, but it becomes very pronounced as the time of heating is increased, as we found on using the electric furnace. A cup heated to 625° for 30 minutes in the furnace was much more alloyed than a similar cup heated to 675° in the same furnace and immediately allowed to cool.

---

[8] This Bulletin, 9, p. 537 (Reprint No. 201); Trans. Am. Electrochem. Soc., 22, p. 372, 1912.

[9] This Bulletin, 9, p. 174 (Reprint No. 194).

[10] Arch. Neer. des. Sci. II, 10, p. 277, 1905; Ann. d. Phys., 19, p. 265, 1906.

[11] Loc. cit., p. 15.

When the deposits are removed from the alloyed cups by electrolysis or nitric acid, a brown stain remains on the platinum if the cups have been heated for only a short time with the flame, or a heavy dark brown or black stain in the case of cups heated for a longer time in the furnace. We were unable to remove this stain completely by scrubbing without a considerable abrasion of the platinum surface, and it persisted even after the cups were carefully washed and dried at 160°. If the cups were heated to bright redness in a Bunsen flame, the slight stains completely disappeared, but their capacity to make trouble was only slightly lessened. Early in our work we found that this change in color from brown or black to gray was accompanied by a marked change in weight of the cup. This change in weight may be as small as one or two tenths of a milligram in the case of cups that have been very slightly alloyed, or it may amount to milligrams in case of heavily alloyed cups. The following figures give the change in weight as we have observed it for a few cases.

TABLE 3

Change in Weight Due to Glowing a Cup Stained by the Alloying of Silver and Platinum After Cleaning and Drying at 160° C

Date	Loss in weight	Character of stain
1915	mg	
July 27	0.180	Very slight brown stains.
	.220	Do.
August 6	.672	Brown stains.
	.643	Do.
September 23	1.083	Brown stains rather prominent.
October 2	4.89	Heavy black stain.

The cause of this phenomenon seems to be the expulsion of adsorbed material in the brown or black stains. These stains we believe to be platinum black. The nature of this material adsorbed by the platinum black has not yet been determined, but experiments will shortly be made to identify it. The disappearance of the stains when heated was more apparent than real since the platinum black was converted into platinum gray, and was therefore hardly visible on the gray surface of the platinum cup itself. The black stains show their marked catalytic power when brought in contact with hydrogen peroxide. Even in cases when the alloying has been so slight that the platinum black stains are invisible we have found that the actual presence of the stains can be shown by making a test with peroxide. In this test the peroxide was made to cover both platinum black and the bare platinum surface of the cup at the top. The bubbles formed quickly in the platinum black region and not noticeably over the bare platinum. There was a sharp line of demarcation between the decomposing peroxide and the remainder at the point where the top of the silver deposit had been. We have also tried this experiment on a cup which had been heavily alloyed by heating in the furnace, and in this case we found that the prominent brown stains caused a great evolution of bubbles in the peroxide. In another case the platinum black stains which had been converted into platinum gray by glowing the cup were tested. Here the effect was much less marked than in a companion cup which had been similarly treated in every way except that it had not been glowed. We think this indicated that the stains were really platinum black.

In the case of moderately alloyed cups with polished inner surfaces the brown stains often showed the position and size and shape of each individual crystal of silver. But as the alloying was increased by longer heating it was possible to see the alloy spread out into the spaces between the crystals of silver, so that when the silver was removed the brown stains had merged together, forming one continuous stain all over the inner surface of the cup. We have examined these stains under a high-power microscope and found them to be essentially a surface phenomenon.

It seemed desirable to investigate the change in weight of this platinum black in its relation to temperature, and therefore we heated a cup to successively higher temperatures, weighing it between each heating. As a trial we washed and weighed it three times, heating it to 151° to see how well the weighings might be expected to repeat themselves. The cup contained only a medium amount of the stain and was not an extreme case.

TABLE 4

Weight of cup minus counterpoise	Temperature	Decrease in weight	Remarks
mg	°C	mg	
+0.276	151	....	Heated in electric oven.
+ .236	151	....	Do.
+ .247	151	....	Do.
+ .123	231	0.130	Do.
+ .044	400	.079	Heated in electric furnace.
− .660	600	.704	Heated in electric furnace. (Color changed to gray.)
− .718	660	.058	Do.
− .830	760	.112	Heated in flame, temperature estimated.
Total....	....	1.083	

These results are shown graphically in Fig. 1.

We next considered the question of the effect this layer of platinum black or platinum gray has upon the silver deposited and what rôle it played in the determination of the inclusions by the method of heating as advocated by Lord Rayleigh and later by Richards. From the above results we concluded that a cup containing a trace of platinum black, on which silver has been deposited, if heated to dull redness, will show a loss in weight that can not properly be assigned to the liberation of inclusions in the silver alone. Yet all previous observers, with little or no precautions to insure against the presence of the platinum black, have assumed the observed loss in weight to represent the liberated inclusion from the silver deposit. It is also obvious that if the platinum black is present, the losses observed when making determinations of the inclusions by heating will be found to be very variable and their magnitude will depend upon the amount of platinum black present and its previous heat treatment. On the other hand, if the cup has been glowed before making the deposit of silver, so that the platinum black is converted to platinum gray, it is less probable that subsequent heating of the silver deposit will show large or variable losses in weight. We have made a special test of this point in the case of two cups both coated with platinum black from previous alloying with silver. One of these was glowed before

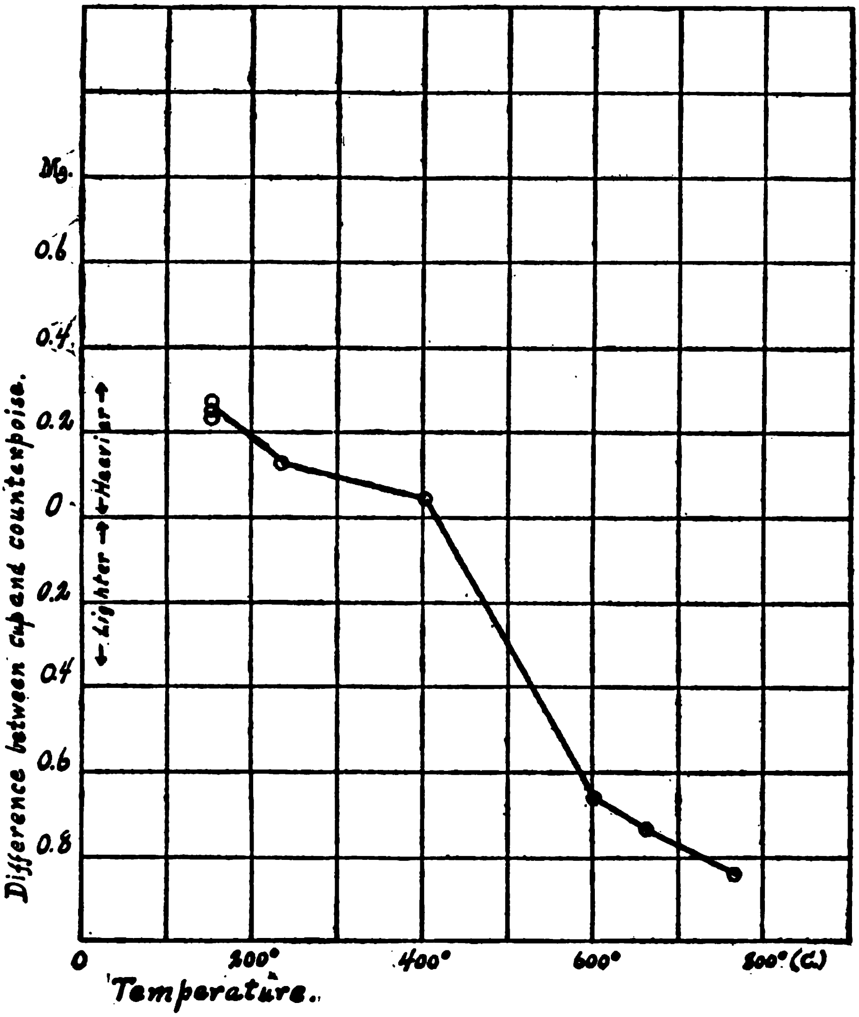


Fig. 1.—*Shows loss in weight of platinum cup containing a stain of platinum black, as the cup was heated to successively higher temperatures. Between 400° and 600°, where the greatest loss occurred, the platinum black changed in color to gray*

making the deposit of silver and the other was treated in the usual way; that is, washed and dried at 160°. Aside from the question of relative weights of the two deposits, which will be discussed further on, we give here the observed losses in weight when the two cups with identical deposits were heated:

Cup that had been glowed before making the deposit lost 0.06 mg.

Cup that had not been glowed lost 4.89 mg.

This, of course, is an exaggerated case, but shows the possibility of error in the assumption made by previous observers as mentioned on page 155.

We concluded that if the cup has been thoroughly glowed previous to making the deposit that a subsequent determination of the inclusions will represent fairly the change in weight of the deposit. For if we take the mean of 13 determinations given in Table 6, in which the cup contained a small amount of platinum black previously glowed, and compare it with 12 determinations made with cups which were entirely free from the platinum black or platinum gray before making the deposit, we find the difference in estimated inclusions to be only 0.0006 per cent, which is within the experimental error.

4. EFFECT OF ALLOYING ON THE AMOUNT OF SILVER DEPOSITED

The first intimation which we had that the presence of platinum black or platinum gray in the voltameter would cause serious errors in the quantity of silver deposited was in an early experiment when two cups that had been heavily alloyed, but subsequently glowed, showed deposits more than 2 mg lighter than the other cups. It was this experiment that first suggested the nature of the stains on the platinum and led us to experiment with them. Since then we have made special experiments to determine the general effect of previous alloying of the cups on subsequent deposits of silver.

TABLE 5

Effect of Platinum Black and Platinum Gray on the Mass of Silver Deposited (Deposits Dried at 160°)

Date	Cup	Deposit	Condition of the cup
1915		mg	
August 12	38	4249.23	Normal voltameter; no alloy.
	27	4249.19	Platinum black removed by aqua regia.
	28	4250.61	A heavy layer of platinum black.
August 18	93	4207.80	Normal voltameter; no alloy.
	92	4207.33	Slightly alloyed and glowed.
	27	4207.68	Platinum black removed by aqua regia.
	39	4207.49	Slightly alloyed and glowed.
	I	4207.58	Platinum black removed by aqua regia.
	II	4207.64	Do.
October 2	27	4233.03	Alloyed and glowed; platinum gray.
	28	4234.35	Heavy layer of platinum black.
	38	4233.58	Normal voltameter; no alloy.

It thus appears that a cup that had been alloyed, and hence contains the platinum black stains, gave an apparently heavier deposit than normal if it had not been glowed or a lighter deposit than normal if it had been glowed previously to making the deposit. This was not understood at first, since we thought that the light weight of the deposit might be due to the catalytic effect of the platinum gray on the hydrogen ions present in the solution, and it was therefore expected in the experiment of August 12 that cup No. 28 would show a still lighter deposit. As a matter of fact, the deposit was much too heavy and this was confirmed by the same cup in the experiment of October 2. The difficulty was explained when we heated cups Nos. 27 and 28 of the last experiment to a dull red.

No. 27 lost 0.060 mg.
No. 28 lost 4.89.

That is, the deposit in No. 28 was in reality much the lightest although apparently heavy owing to material probably adsorbed by the platinum black.

Careful measurements of the acidity of the electrolyte were made and checked for the experiment of October 2. It was found that the acidity increased considerably in the case of the cup with platinum black, somewhat less for the cup with platinum gray, and none at all for the standard cup.

The acidities were as follows:

Initial acidity of electrolyte	7×10^{-6} acid
Final acidity No. 27, platinum gray	10×10^{-6} acid
Final acidity No. 28, platinum black	15×10^{-6} acid
Final acidity No. 38, normal cup	6×10^{-6} acid

The Table 5 shows that when the platinum cup containing the platinum black is cleaned with cold concentrated aqua regia and rubbed the deposits are in agreement with those in cups which have never been alloyed with silver. This cleaning process, however, removes a considerable amount of the platinum. In exaggerated cases this is as much as a gram. For this reason it appears doubtful whether a moderate amount of scrubbing would suffice for the complete elimination of the platinum black. Richards and Anderegg, for example, mention scrubbing the cups and say that the crucibles lost a few tenths of a milligram each time. Our work would lead us to expect a much greater loss than this if the platinum black, even for only a slight alloying, be entirely removed.

Cleaning the cups in this way is inconvenient and destructive to the cup. We do not find it necessary to make inclusion determination for every deposit of silver and to do so would speedily ruin the platinum cups.

5. ESTIMATION OF INCLUSIONS IN DEPOSITS FROM PURE ELECTROLYTES

Table 6 shows the observed losses in weight of deposits from pure electrolytes, the purity being judged by the standards of purity previously published by the Bureau.[12] All such deposits which were heated according to the method described by Richards and Anderegg are included in this table. In no case was platinum black present, but in some cases slight amounts of platinum black had been converted over into platinum gray before making the deposits. This is immaterial, as we showed on page 157, but these cases are noted in the table. All deposits which were heated in the electric furnace are also included in the table with the exception of two in the experiment of July 20. For unknown reasons these were discordant with all the other results of the table, and they are therefore omitted. If, however, they had been included they would have affected the mean result by only 0.0005 per cent.

---

[12] This Bulletin, 9, p. 524 Reprint No. 201.

TABLE 6

Estimation of Inclusions by Heating the Deposits

Date	Cup	Method of heating	Temperature	Number of heatings	Total loss in weight	Percentage loss in weight	Platinum gray present or not	Remarks
1915			Deg. C		mg			
June 14	95	Flame		2	0.130	0.0032	No	Silver nitrate prepared by Bureau of Standards methods.
	39	...do...		2	.186	.0045	No	Do.
June 16	95	...do...		3	.220	.0055	Yes	Do.
	39	...do...		3	.300	.0075	Yes	Do.
June 24	95	...do...		3	.181	.0041	Yes	Silver nitrate as purchased not quite pure.
	92	...do...		3	.129	.0029	No	Silver nitrate prepared by Bureau of Standards methods.
	27	...do...		3	.205	.0047	No	Do.
	28	...do...		3	.279	.0064	No	Silver nitrate as purchased not quite pure.
July 9	95	...do...		2	+.007	+.0002	Yes	Silver nitrate prepared by the Princeton method.
	92	...do...		2	.013	.0003	Yes	Do.
	27	Furnace.	625	2	.048	.0011	Yes	Do.
	28	...do...	625	2	.028	.0007	Yes	Do.
	I	...do...	625	2	.166	.0040	No	Silver nitrate prepared by the Princeton method (cup not previously glowed).
	II	...do...	625	2	.115	.0028	No	Do.
July 20	95	Flame		1	.161	.0037	Yes	Silver nitrate prepared by the Princeton method.
	92	...do...		1	.116	.0027	Yes	Do.
	I	Furnace.	623	1	.322	.0073	Yes	Do.
	II	...do...	623	1	.254	.0058	Yes	Do.
August 9	92	Flame		1	.333	.0079	Yes	Do.
August 18	27	Furnace.	625	1	.240	.0057	No	Do.
	I	...do...	630	1	.111	.0026	No	Do.
	II	...do...	625	1	.169	.0039	No	Do.
October 2	27	Flame		1	.060	.0014	Yes	Silver nitrate prepared by Bureau of Standards methods.
October 13	27	...do...		1	.251	.0057	No	Do.
	28	...do...		1	.238	.0054	No	Do.
Mean [a]						.0040		

[a] Average deviation of a single observation, ±0.0018 per cent; probable error, 0.0015 per cent for single observation; probable error, 0.0003 per cent for mean result. Percentage loss in weight, mean flame determinations, 0.0041 per cent; percentage loss in weight, mean furnace determinations, 0.0038 per cent.

The inclusions expelled by heating the silver, therefore, seem to be about 0.004 per cent. Richards and Anderegg[13] apply a correction of 6 per cent for the solids they estimate to remain from the inclusions, but 6 per cent of 0.004 per cent is too small to consider.

It is interesting at this point to compare the results which have previously been obtained by methods similar to those used in this paper. We give in Table 7 an analysis of earlier results compared with our own. In general, these results had to be computed from the original data contained in the various papers. Thus, in the case of Lord Rayleigh's Table 2, we have computed the percentage loss in weight of the deposit for all deposits made from silver nitrate not contaminated with acetate. For Richards and Anderegg's work we have included all the results given in their Table 3 and have averaged them together.

TABLE 7

Summary of Results Obtained by Heating the Silver Deposits in the Platinum Cups to Expel Inclusions

Year	Observers	Extreme values		Range	Mean result	Observations	References
		Minimum	Maximum				
		Per cent	Per cent	Per cent	Per cent		
1884	Rayleigh and Sedgwick..	0.000	−0.030	0.030	0.010	24	Phil. Trans. A., 175, p. 438.
1902	Richards and Heimrod..	− .003	− .030	.027	.018	12	Zs. f. Phys. Chem., 41, p. 323.
1906	Van Dijk................	+ .009	− .006	.015	.000	7	Ann. d. Phys., 19, p. 266.
1908	Jaeger and von Steinwehr.	+ .002	− .005	.007	.0008	18	Zs. f. Instrk., 25, p. 226.
1912	Boltzmann..............	+ .0026	− .0087	.0113	.0023	19	Sitzber. Akad. Wiss., Wien, 121, p. 1062.
1915	Richards and Anderegg..	− .0039	− .0352	.0313	.0142	27	J. Am. Chem. Soc., 37, p. 16.
1915	Vinal and Bovard........	+ .0002	− .0079	.0081	.0040	25	This paper.

It is readily seen from Table 7 that the results classify themselves in two groups. On the one hand, we have Lord Rayleigh and Mrs. Sedgwick, Richards and Heimrod, and Richards and Anderegg; on the other hand, we have Van Dijk, Jaeger and von Steinwehr, Boltzmann, and the present authors. So far as Lord Rayleigh and Mrs. Sedgwick are concerned, it must be remembered that they were working with the filter paper voltameter, and therefore their electrolyte was impure, which we think will account for a high value for the inclusions. Whether we include their results or not, the fact remains that Richards and his coworkers stand alone in finding the largest inclusions and in having the largest variation between their extreme values. The most consistent results—that is, those having the smallest difference between the extreme values—are the results of Jaeger and von Steinwehr. These are closely followed by the results of the present paper and by the results of Boltzmann and Van Dijk. If we group these four series together, we have 69 fairly consistent determinations of the inclusions of which the mean is 0.0023 per cent, weighting each of the four results according to the number of observations on which it is based. Richards's 39 observations, on the contrary, give a mean result of 0.0154 per cent, or nearly seven times larger than the mean of the other observers. Just how much effect the platinum black has had in the results of these previous observers we shall not attempt to say, but it is evident that in the case of Van Dijk, Jaeger and von Steinwehr, and Boltzmann it was very small. The last named mentions glowing the cup each time before making a deposit, and this would nullify the effect of the platinum black so far as determining the inclusions is concerned, as we have shown.

---

[13] Loc. cit., p. 18.

The voltameters used in the researches that showed very small inclusions have varied greatly in size. The smallest cup was Van Dijk's, which held only 30 cc, and the largest were our own, some of which held over 300 cc.

Smith Mather and Lowry heated a few deposits, but not to as high a temperature as in the case of the results recorded in Table 7; they are therefore not mentioned in this connection. This is also the case with a few other observers whose methods have differed in principle from the methods of this paper.

6. THE VALUE OF THE FARADAY

The Bureau [14] published some years ago a value for the absolute electrochemical equivalent of silver which was obtained by the same silver voltameters used in the present work and an absolute current balance. This value was 1.11804 mg per coulomb. Subsequently this was revised [15] to 1.11805 mg per coulomb. Which-ever of these values is taken, if we apply as a correction the estimated inclusions as found in the preceding section it appears that 1.11800 mg per coulomb which was adopted by the London Electrical Congress of 1908 as the value for the electrochemical equivalent is in reality the closest figure that we can assign to this constant, and seems to be correct to within a few parts in one hundred thousand. We do not know the value for the atomic weight of silver with this degree of accuracy. It is only expressed to five significant figures, but taking the present international value 107.88 we find the value of the Faraday to be

---

[14] This Bulletin, 8, p. 367 (Reprint No. 171).

[15] This Bulletin, 10, p. 477 (Reprint No. 220).

96 494

In a recent paper by Vinal and Bates [16] the value of 96 500 is recommended for general use, and this recommendation still holds good. The correction for inclusions found in the present paper will account for only 4 out of 21 parts in 100 000 difference between the results of the silver and iodine voltameters of their work. Additional experiments are now being made in the Princeton laboratory in which some of the deposits obtained during the present investigation will be analyzed. After these results have been obtained a more extensive discussion of the Faraday will be given.

7. ADDITIONAL EXPERIMENTS ON THE DEPOSITS

Successive Heatings of the Deposits.—It will be noted in Table 6 that some of the deposits were heated more than once. This was to determine how completely the inclusions are expelled by one heating. Our experiments showed that about 90 per cent of the total loss in weight occurs the first time that they are heated.[17] The second and third heatings show small changes which are sometimes slight gains in weight instead of losses.

Effect of Heating Deposits to an Abnormally High Temperature.—Two deposits were heated by a flame to a temperature estimated at 700° C after being heated to dull redness. The resulting loss in weight was observed:

	Percentage of deposit
	0.0017
	.0006
Mean	.0011

---

[16] This Bulletin, 10, p. 449 (Reprint No. 218).

[17] Boltzmann (loc. cit.) also obtained a similar result.

One deposit was heated in the furnace to 675° after having been twice heated to 625°; the result was an apparent gain in weight of 0.0011 per cent.

Effect of Prolonged Heating of the Deposit.—When the deposits are heated with the Bunsen burner the time that the deposit is at a high temperature is very brief, but in the case of the furnace the cup and deposit are over 600° for at least seven minutes. The agreement of these two methods of heating shows that the time is not significant, but as a further test we baked a deposit for the second time in the furnace for one-half hour at 625° and found the loss in weight to be only 0.0004 per cent.

It is fortunate that the time for heating can be made so short because the trouble with the alloy of silver and platinum is much lessened.

Heating the Deposit After Removal from Cathode.—Two samples A and B, of silver deposits from pure electrolytes were removed from the silver cathodes as described on page 151. These were dried at 160° in a small platinum dish previously washed, dried, and glowed. After weighing they were heated in the same platinum dish to dull redness with a Bunsen burner. We give in Table 8 these two values, together with the values obtained by heating the deposits on platinum of the same run according to the method described by Richards or in the furnace. Two deposits of the run of July 9 which are given in Table 6 are omitted here because the platinum cups were not previously glowed, and two deposits also on June 24 made with a different electrolyte.

TABLE 8

Estimations of Inclusions in Silver Scraped from the Cathode

Date	Sample	Loss in weight	Cup	Loss in weight	Mean	Difference, sample minus cup
1915		Per cent		Per cent	Per cent	Per cent
June 24..............................	A	0.0045	92	0.0029	0.0038	+0.0007
			27	.0047	....	....
July 9..............................	B	0008	95	(+).0002	....	....
			92	.0003	....	....
			27	.0011	.0005	+0.0003
			28	.0007	....	....

The agreement of these two results is better than was to be expected.

The Inclusions Between the Crystals and the Surface of the Cup.—Richards and Anderegg [18] note that platinum cups with rough interior surfaces considerably increase the inclusions. It therefore seemed worth while to examine this point closely because of the excellent agreement of results obtained by Hulett and Vinal,[19] although one used platinum cups with rough interior surfaces and the other smooth surfaces. In the present work cups I and II had rough interior surfaces and 27 and 28 became roughened after cleaning with the aqua regia, so we may readily classify the results given in Table 6 according to the character of the interior surface of the cup. This is done in Table 9.

TABLE 9

Comparison of Inclusions in Voltameters with Rough and Smooth Surfaces

Smooth surfaces (per cent loss in weight on heating)	Rough surfaces (per cent loss in weight on heating)
Per cent	Per cent
0.0032	0.0040
45	28
55	73
75	58
41	57
29	26
47	39
64	14
+02	57
08	54
11	..
07	..
37	..
27	..
79	..
Mean .0037	.0044

The difference is thus only 0.0007 per cent, which is within the experimental error, and therefore we may say that the inclusions on smooth and rough surfaces are, so far as our experiments go, the same.[20]

---

[18] Loc. cit. p. 16.

[19] This Bulletin 11, p. 557 (Reprint No. 240).

As to the magnitude of the inclusions between the crystals and cup we were enabled to form an estimate using the silver cups in which the silver can be so easily scraped from the cathode while the cup is filled with conductivity water.

The general procedure was to wash these deposits until further washing produced no change in the conductivity of the water used. Then a platinum cup similar to the cups in use was filled after washing with the same conductivity water and stood beside the cup under test. A large glass plate was interposed between the observer and the cups while the silver was scraped down so that during the three to five minutes required the breath of the observer might not contaminate the water in the cups. As soon as the scraping was complete the conductivity of the water in the cup under test, and the blank also, were immediately measured in a conductivity cell of the pipette form.[21] The net result found represents the increase due to the silver nitrate liberated by scraping the silver, and also all other causes of increase of conductivity, except the effect of temperature, which was under control. Consequently the values found are maximum values and the silver nitrate calculated from the increase in conductivity is probably too large. In the first experiment the value found is considerably larger than in the others. This is probably due to imperfect technique before we learned the best way of doing the experiment. The results are given in Table 10.

TABLE 10

Inclusions Between Crystals and Cup

Date	Cup	Equivalent $AgNO_3$ for increase in conductivity
1915		mg
August 9	VI	0.04 (omitted from mean).
	V	.01
August 18	V	.0052
	VI	.0078
Mean	......	.0076 ≎ 0.0002 per cent of the deposit.

---

[20] Compare, Jaeger and von Steinwehr, Zs. f. Instrk., 85, p. 233; 1915.

[21] This was the same cell used by Hulett and Vinal, This Bulletin, 11, p. 558 (Reprint No. 240).

The amount of silver nitrate trapped behind the crystals is therefore very small, and consequently it is not surprising that Table 8 shows so close an agreement between the inclusions determined for the silver removed from the cathode and otherwise.

Inclusions in Silver Deposits from Less Pure Electrolyte.—In two experiments we used electrolyte manifestly less pure than in the other experiments. For one of these we purposely added filter paper to the electrolyte and in the other the impurity manifested itself by a considerable volume effect, which, being larger than the average experimental error, we regard as evidence of impurity. These results are given in Table 11.

TABLE 11

Estimated Inclusions by Heating the Cups with Deposits from Impure Electrolytes

Date	Cup	Percentage loss in weight	Remarks
1915			
July 2	95	0.0067	Filter paper put in electrolyte.
	92	.0118	Do.
	27	.0071	Do.
	28	.0097	Do.
July 28	95	.0106	Volume effect of 7 in 100 000.
	92	.0102	Do.
	27	.0118	Do.
	28	.0095	Do.
	I	.0102	Do.
	II	.0093	Do.
Mean	......	.0097	

The inclusions, therefore, appear to be more than twice what was found in the case of pure electrolyte. This is in accord with the view expressed by the Bureau[22] several years ago that the presence of impurities of a colloidal nature which break up the crystalline structure of the silver will increase the inclusions in the deposited silver.

The Volume Effect.—Richards and Anderegg,[23] explaining the volume effect, attribute it to a surface effect and claim the inclusion to be greater in the larger cups, so that when both large and small cups are heated the resultant deposits are in agreement. We have examined all our experiments with this point in view, and we give in Table 12 an analysis of all those in which a comparison of our large and small cups (No. 92 and No. 95 large size, No. 27 and No. 28 small size) was made with subsequent heating, except for the experiment of July 20, in which, as we stated on page 159, the results with the small cups were anomalous. This table includes the results of deposits from pure solutions in which the volume effect was very small or absent altogether and also the results of deposits from impure solutions in which the volume effect is large. The table shows that heating the deposits to expel the inclusions did not make the difference between large and small deposits any less,[34] as Richards's theory would call for, but, on the other hand, the difference became a trifle larger, on the average 0.03 mg for each comparison, which is perhaps as good agreement as could be expected. Richards's results could, however, be explained on his theory by the assumption that the platinum black from previous heatings was not entirely eliminated before making the deposit. In such a case for two cups equally alloyed the amount of platinum black would be proportional to the surface of the cup. This, even with pure electrolyte, would probably show an apparently heavy deposit in the large cup, as our results on page 158 indicate, and this cup would also lose the most on heating to a high temperature, hence the two deposits would appear to draw together. The results of Table 12 emphasize the previous viewpoint of the Bureau that the purity of the salt used for the electrolyte is the determining factor in the volume effect.

---

[22] This Bulletin, 10, p. 517 (Reprint No. 220).

[23] Loc. cit., p. 16.

---

[34] Examining the results of Lord Rayleigh and Mrs. Sedgwick, we find the same thing. Their large cup deposits lost 0.013 per cent and their small cup deposits lost 0.009 per cent. The difference between these results is well within their experimental error.

TABLE 12

Analysis of Deposits with Reference to the Volume Effect

Date	Size	Deposit before heating	Δ Large-small	Deposit after heating	Δ Large-small	Remarks
1915		mg	mg	mg	mg	
June 14	Large	4095.69	+0.12	4095.56	+0.17	
	Small	4095.57		4095.39		
June 16	Large	3975.84	+ .21	3975.62	+ .29	
	Small	3975.63		3975.33		
June 24	Large	4375.07	+ .07	4374.94	+ .14	
	Small	4375.00		4374.80		
	Large	4375.25	+ .15	4375.07	+ .25	Silver nitrate as purchased
	Small	4375.10		4374.82		Do.
July 2	Large	4221.87	+ .97	4221.59	+ .99	Filter paper in electrolyte. Note volume effect
	Small	4230.		4220.60		Do.
	Large	4222.	+1.53	4221.98	+1.46	Do.
	Small	4220.93		4220.52		Do.
July 9	Large	4180.13	± .00	4180.14	+ .06	
	Small	4180.13		4180.08		
	Large	4180.09	− .04	4180.08	− .02	
	Small	4180.13		4180.10		
July 28	Large	4339.94	+ .28	4339.48	+ .33	
	Small	4339.66		4339.15		
	Large	4339.84	+ .34	4339.40	+ .31	
	Small	4339.50		4339.09		
Total Δ's			+3.63		+3.98	

8. EXPERIMENTS ON THE ANODE LIQUID

Many lines of evidence led the Bureau to the conclusion stated in its Part[25] 1 of the recent voltameter papers that the effects of the supposed anomalous substance formed at the anode during electrolysis were in reality due to impurities present in the solution, as, for example, filter paper. The Bureau has not found it necessary to change this view, but in the present work we have tried two further experiments on the anode liquid.

The first experiment was suggested to us by the remark of Richards and Anderegg[26] that the reason most observers had failed to find this peculiar compound in the anode liquid is because they delayed testing for it until the compound had become oxidized and vanished. Accordingly, we drew four 10 cc samples of the dense anode liquid (17 per cent, the original electrolyte was 10 per cent) from inside the porous cups of the voltameters of August 18. The electrolyte of this experiment was quite pure as judged by the permanganate, acidity, and volume effect tests. The four samples of anode liquid were taken within one minute after the electrical circuit was broken. Each was put in a stoppered glass tube and acidified, then 1 cc of N/1000 $KMnO_4$ was added to each tube and all shaken to mix the contents. The whole operation consumed less than five minutes. The times required for the permanganate color to fade were noted. They were

---

[25] This Bulletin, 9, p. 151 (Reprint No. 194).

[26] J. Am. Chem. Soc., 37, p. 686: 1915.

42 minutes
52 minutes
70 minutes
70 minutes
mean, 59 minutes

We do not think that our anode liquid contained the oxidizable compound spoken of by Richards, else the color of so small a quantity as 1 cc of N/1000 $KMnO_4$ would hardly be expected to last for an hour.

Our second experiment on the anode liquid was suggested by the use of the alundum porous cups in an experiment described by Richards and Anderegg.[37] They used the porcelain porous cup to hold back the anode compound and the very porous alundum cup to let it through. We thought that a slightly different arrangement of the porcelain and alundum cups would perhaps throw more direct light on the matter. A previous experiment showed that our alundum cups permitted water to pass through the pores about 60 times as fast as it passed through our porcelain (Pukal) porous cups.

We arranged three voltameters. One was a normal voltameter with the ordinary porous cup, the second was similar to the first except that an alundum porous cup was used in place of the porcelain porous cup. The third had a porcelain porous cup fitting snugly inside of an alundum porous cup. The alundum and porcelain cups were all prepared similarly and as described by the Bureau.[28] According to the theory of Richards the first and third voltameters should agree and both give lighter deposits than the second; but, on the other hand, if the heavy anode compound with excess silver is nonexistent then the second and third should agree, and if these deposits are heavier than that in the first it would show that the alundum cups are responsible for introducing impurities into the solution. The results of this experiment were as follows:

---

[37] J. Am. Chem. Soc., 37, p. 685; 1915.

	mg
The first (normal voltameter)	4327.08
The second (alundum cup)	4327.38
The third (alundum cup with porcelain porous cup inside)	4327.44

These results, therefore, tend to confirm the previous views of the Bureau that the anode reactions produce no effect whatever in the quantitative measurements [29] of the silver deposited.

This work has been done at the Bureau of Standards under the direction of Dr. E. B. Rosa. We have also been fortunate in having the help of Prof. G. A. Hulett. The investigation is being continued under the direction of Prof. Hulett by one of the present authors (Bovard) in the Princeton laboratory.

9. SUMMARY

1. We have heated a number of silver deposits to temperatures slightly above 600°, both with a flame and in an electric furnace, and have found the losses in weight to indicate inclusions of foreign matter in the deposits to be 0.0040 per cent on the average for pure electrolyte and higher for impure electrolytes.

2. We have found that such heating of the deposits produces an alloy of silver and platinum, which on dissolving out the silver leaves a layer of platinum black that may lead to serious errors the next time the cup is used if proper precautions are not taken.

3. We are led to conclude that the most accurate absolute value for the electrochemical equivalent of silver is 1.11800 mg per coulomb, and therefore the value of the Faraday becomes 96 494 coulombs, but for general purposes 96 500 as a round number is recommended.

---

[28] This Bulletin, 9, p. 185 (Reprint No. 194).

[29] Boltzmann (loc. cit.) made experiments on the anode liquid and also found it without effect on the deposited silver.

4. Inclusions in silver deposits made on smooth platinum surfaces are the same to within the experimental error as when deposits are made on matte surfaces.

5. Inclusions between the crystals and cup have been measured by an application of the conductivity method and are found to be a neglible part of the total inclusions, which with pure solutions were about four parts in a hundred thousand.

6. In cases where the deposit in large cups exceeds that in small cups (that is, where the "volume effect" is appreciable) we do not find that strong heating of the deposits diminishes the difference.

7. Two experiments on the anode liquid support the Bureau's previous conclusions as to the nonexistence of the heavy anode ion.

WASHINGTON, October 20, 1915.

⁂

CORRELATION OF THE MAGNETIC AND MECHANICAL PROPERTIES OF STEEL

By Charles W. Burrows

CONTENTS

	Page
I. Purpose and scope of paper	173
II. Relation of the magnetic to the other characteristics of steel	175
III. Magnetic behavior of steel under the influence of mechanical stress	182
1. Résumé of early work	182
2. For stresses below the elastic limit	184
3. For stresses greater than the elastic limit	188
(a) Experiments of Fraichet	189
IV. Inhomogeneities and flaws	200
1. Inhomogeneities in steel rails	203
V. Conclusions	207
VI. Bibliography	209

I. PURPOSE AND SCOPE OF PAPER

So much work on this subject has been done during the last few years that the prospects are very bright that a magnetic examination of steel will furnish information of practical value as to its fitness for mechanical uses, without at the same time injuring or destroying the specimen under test.

This paper is a review of the work done in correlating the magnetic and mechanical properties of steel. The International Association for Testing Materials has designated this as one of the important problems of to-day and has assigned its investigation to a special committee. A number of investigators are actively engaged on this problem.

Among the mechanical properties that have been studied in connection with the magnetic characteristics are hardness, toughness, elasticity, tensile strength, and resistance to repeated stresses. The well-known fact that not only do these various properties depend upon the chemical composition and the heat treatment, but that frequently very slight changes in the chemical composition or the heat treatment produce very appreciable effects on the magnetic and mechanical properties complicates the problem considerably.

The numerical data of this paper are taken substantially as they were presented by the original investigators. It is not to be assumed that the data are of great importance as absolute values of the various constants in question. In very few cases have pure materials been available for the investigators. Frequently the methods of measurement are open to objection and essential conditions of the experiment are not recorded. For example, the amount of manganese in a carbon steel may be undetermined and the heat treatment uncertain, although their influence is comparable in magnitude with that of carbon. However, as the purpose of this paper is to show that changes in conditions produce corresponding changes in both the magnetic and the mechanical properties, uncertainties in the absolute values will not vitiate their usefulness for this purpose.

There are at least three phases of this subject that warrant consideration. Of first importance is the comparison of the magnetic properties with the other physical properties of the material. If it can be shown that every variation in composition and method of preparation brings with it a corresponding variation in magnetic characteristics, and, further, that variations in magnetic conditions are always accompanied by other physical variations, then it is obvious that the general physical characteristics may be defined in terms of the magnetic constants. Whether such a procedure is feasible depends upon the fullness of our knowledge of the simultaneous magnetic and mechanical data and also upon the facility with which the necessary magnetic data are obtainable.

A second important phase of this subject is the variation in magnetic behavior as the test piece is subjected to the influence of stress. The correlation here is so close that the strains set up in a stressed bar are accompanied by simultaneous variations in the magnetic behavior which change in character as the magnitude of the strain with respect to the elastic limit changes.

Finally, mechanical inhomogeneities of whatever origin are mirrored by corresponding magnetic inhomogeneities. A magnetic test may therefore be of assistance in detecting flaws in material where the vital characteristic is reliability.

II. RELATION OF THE MAGNETIC TO THE OTHER CHARACTERISTICS OF STEEL

A number of experiments have been made which show a rather close connection between the magnetic characteristics and the chemical constitution. The following four curves are taken from the data of Gumlich:[1]

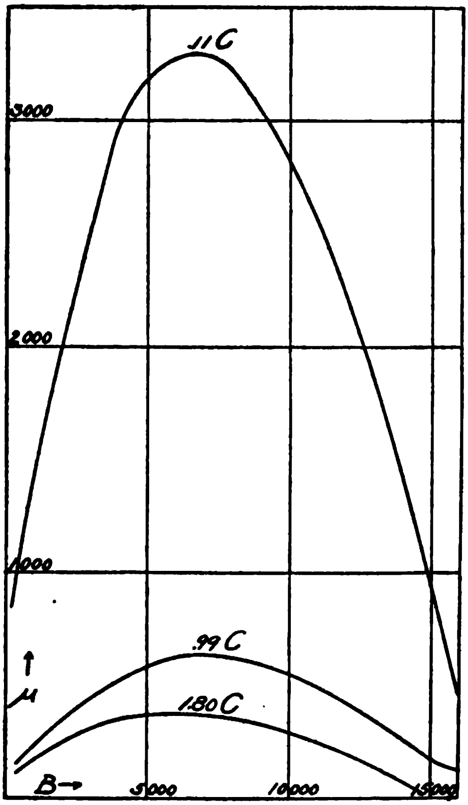


FIG. 1.—*Showing the variation of permeability with induction for steels of different carbon content*

Fig. 1 shows how the permeability varies throughout the course of the magnetization curve for different carbon content. This and other experimental work indicate that for a complete series of iron-carbon alloys, with no other differences than their carbon content, the carbon content is indicated by the permeability curve.

---

[1] Gumlich, "Magnetic properties of iron-carbon and iron-silicon alloys," Faraday Society Transactions, 8, pp. 98–114; 1912.

Fig. 2 shows the connection between the saturation values of magnetic induction (that is, the maximum values of $B-H$) and the carbon content. Pure iron has the highest saturation value for the series. An addition of carbon causes a decrease in the magnetization at a rate almost proportional to the amount of carbon added. This simple relation between the saturation value and the carbon content holds for any particular heat treatment. For different heat treatments, however, the saturation value changes with the carbon content at different rates. A comparison of the two curves shows that the reduction due to the presence of carbon is less for the annealed than for the quenched.

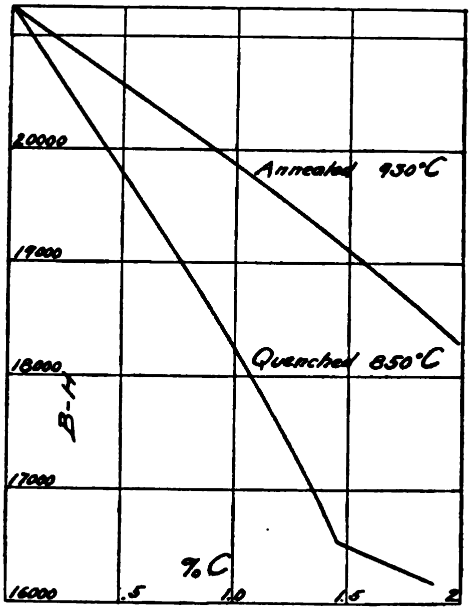


FIG. 2.—*Showing the magnetic saturation values of steels of different carbon contention the annealed and in the quenched conditions*

Fig. 3 shows the influence of carbon on the coercive force. Annealed steel has a coercive force which increases linearly with increase in carbon until an approximately eutectic alloy is reached.

For higher carbon contents the coercive force still increases linearly but at a decreased rate. Steel quenched at 800° C. shows a linear increase in coercive force for the hypoeutectic alloys and constant coercive force for the hypereutectics. Quenching at higher temperatures results in more complex relations.

Other elements than carbon will reduce the saturation value. Fig. 4 shows the rate of reduction of the saturation value for various additions of silicon. Here also the relation between the reduction in the saturation value and the percentage of alloyed element is nearly linear.

Waggoner[2] shows that magnetic hysteresis and the maximum strength of steels vary in the same way with changing carbon content. The characteristic curves of magnetic and elastic hysteresis show a marked similarity of shape. A comparison of the curve showing the relation of elongation under stress (or ductility) to the carbon content with the corresponding curve of magnetization and carbon content shows a striking similarity, indicating that the ductility of these alloys and their intensity of magnetization are affected in the same way by the chemical com-

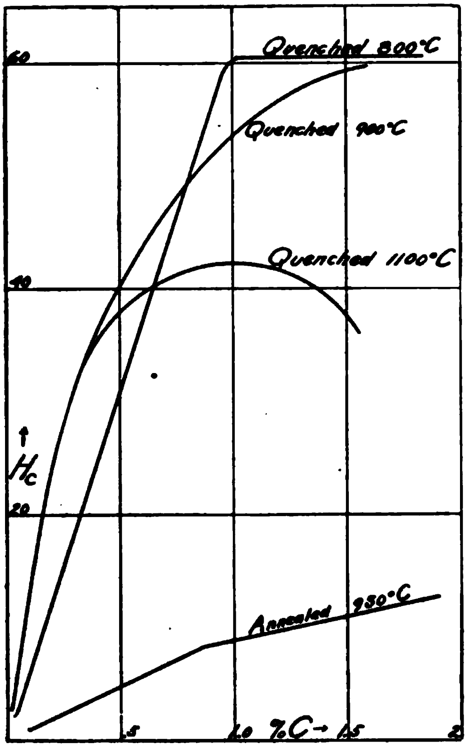


FIG. 3.—*Showing the variation of coercive force with carbon content for different heat treatments*

position. The maximum susceptibility-carbon curve is also similar to the curve of ductility-carbon—that is, the maximum susceptibility decreases with increasing carbon until the eutectic is reached and then again increases with increase in carbon content.

---

[2] Waggoner, "A relation between the magnetic and the elastic properties of a series of unhardened iron-carbon alloys," Phys. Rev., 35, pp. 58–65; 1912.

Mars[3] shows that for a series of iron-carbon alloys there is a definite relation between the Brinell hardness and the residual induction as shown in Fig. 5.

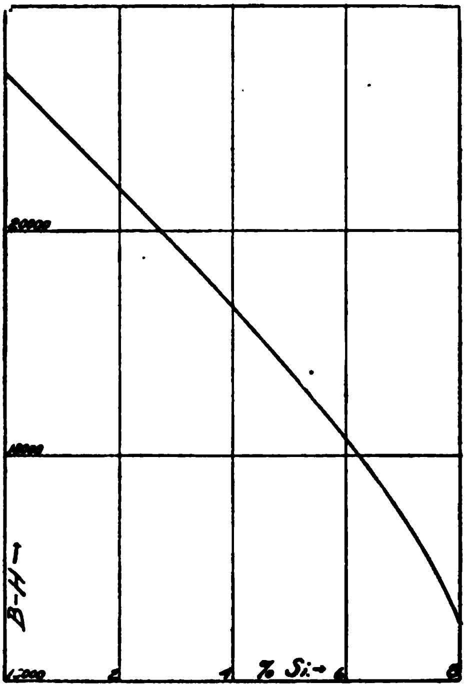


Fig. 4.—*Showing the variation of the magnetic saturation value with percentage of silicon in iron-silicon alloys*

Goerens[4] has shown the changes which the magnetic characteristics of a cold-worked steel undergo after various annealings. This steel was cold-drawn in five steps from an initial diameter of 7 mm to a final diameter of 2.7 mm. Fig. 6 shows the variation of the magnetic constants after annealing at various temperatures. Fig. 7 shows the corresponding mechanical characteristics. The mechanical properties are decidedly different for annealings below and above 500°. The same is true for the curve of maximum permeability. The curve of residual induction shows

---

[3] Mars, Stahl und Eisen, 29, pp. 1673–1678; 1909.

[4] Goerens, Stahl and Eisen, 34, pp. 282–285; 1914.

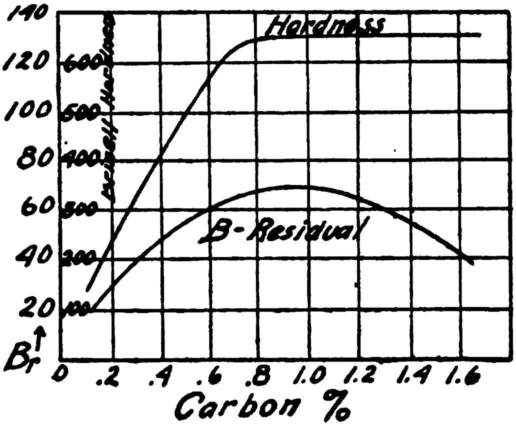


FIG. 5.—*Showing how the mechanical hardness and the residual induction vary with carbon content*

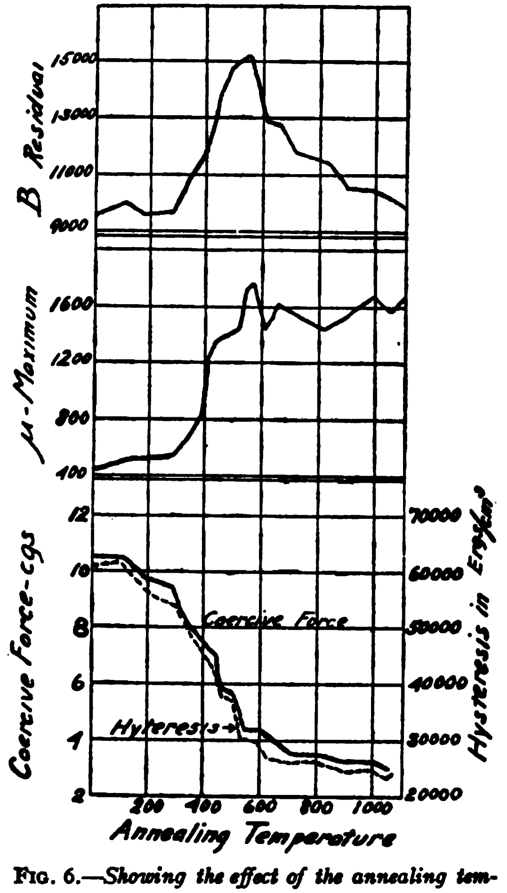


FIG. 6.—*Showing the effect of the annealing temperature on the magnetic properties of a mechanically hardened steel*

a sharp maximum at 500°. The curves for coercive force and hysteresis show steady decreases with increase of annealing temperature. In general, the magnetic characteristics respond to the annealing process in just as definite a manner as do the mechanical properties. In fact, it would be easier to deduce the heat treatment from the magnetic data than from the mechanical.

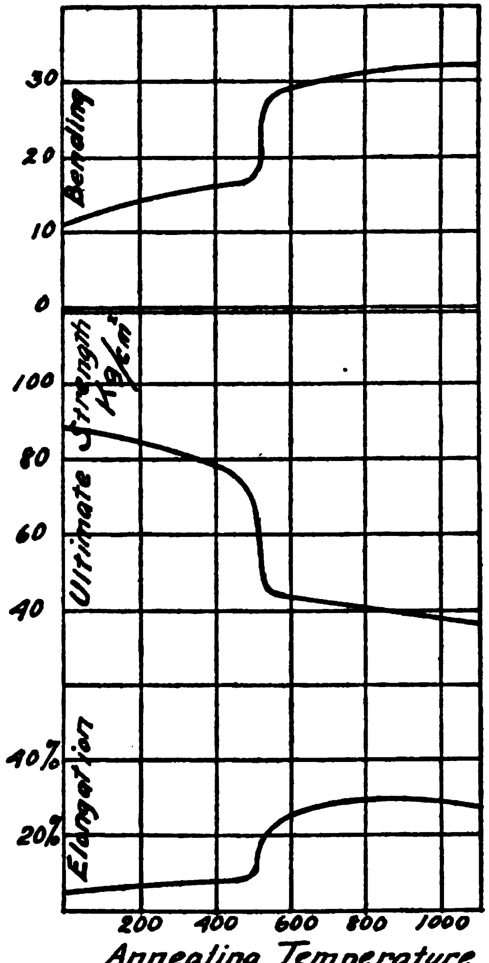


Fig. 7.—*Showing the effect of the annealing temperature on the mechanical properties of a mechanically hardened steel*

Fig. 8 may be considered as typical of the magnetic behavior of many alloy steels. The usual effect of quenching is to lower the induction curve. Subsequent drawing raises the curve again.

This improvement in the permeability increases with increase in drawing temperature up to a certain maximum when the curve occupies approximately the position of curve *C*. Higher drawing temperatures cause a reduction in the permeability and the curve approaches approximately the position of the annealed material.

Each curve corresponds to a given heat treatment and also to rather definite mechanical properties. The material of curve *B* is so brittle that it is not usable, while that of curve *A* has a large angle of cold bend, but does not possess sufficient strength. The material of curve *C* has an ultimate strength several times that of curve *A*, accompanied by a fair degree of toughness. Not only do the normal induction curves show the characteristic effects of heat treatment, but also the residual inductions and the coercive forces after a magnetizing force of 150 gausses show such effects. It is possible to obtain a quenched and drawn steel whose induction curve approaches closely the position of the annealed curve.

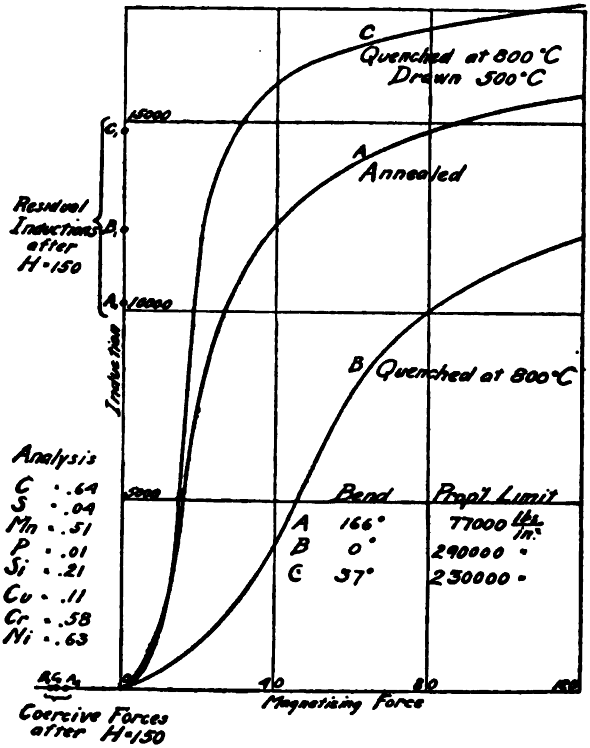


FIG. 8.—*Characteristic induction curves of an alloy steel*

However, two such steels would be at once differentiated by their differences in residual induction and coercive force.

Fig. 9 shows a set of characteristic curves for a spring steel of approximately 1 per cent carbon. Here, as in the case of the alloy steel, a high ultimate strength, coupled with a fair degree of toughness, is characteristic of those curves of Figs. 8 and 9 which are steep and of relatively high permeability.

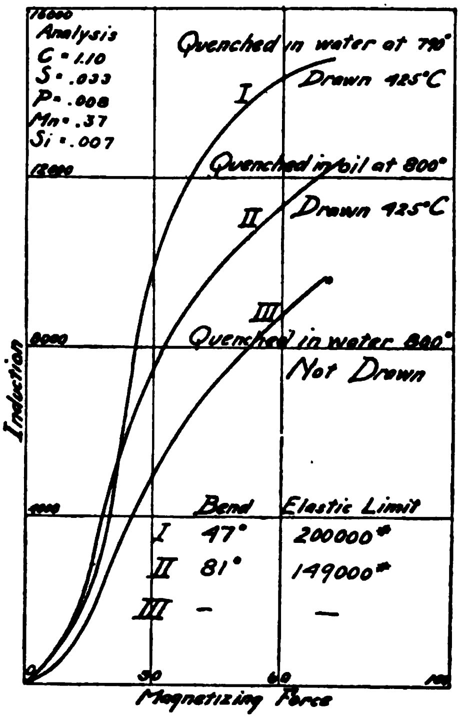


FIG. 9.—*Characteristic curves of a carbon steel*

Fig. 10 shows the magnetic characteristics of a low-carbon steel after various forms of heat and mechanical treatment. The similarity between the hardening effects of cold working and of quenching is shown by the similarity of the magnetic curves.

III. MAGNETIC BEHAVIOR OF STEEL UNDER THE INFLUENCE OF MECHANICAL STRESS

1. RÉSUMÉ OF EARLY WORK

Matteuci in 1847 noticed that the magnetization of a permanent magnet was increased when the bar was subjected to tension.

Villari showed in 1868 that the permeability of a bar of steel was altered when the specimen was subjected to tension. For low inductions this change is an increase in permeability, while for high inductions it is a decrease. The value of the induction at which tension does not alter the permeability is the "Villari reversal point." The permeability is modified by tension whether the tension is applied first and then the magnetizing force or vice versa. The effect is noticeable even after the tension has been applied and removed before the magnetizing force is applied. The effects of tension in these three cases differ in magnitude rather than in nature. The effect is present whether a constant tension is applied while the magnetizing force is varied or a varying tension is applied to a specimen under a constant magnetizing force.

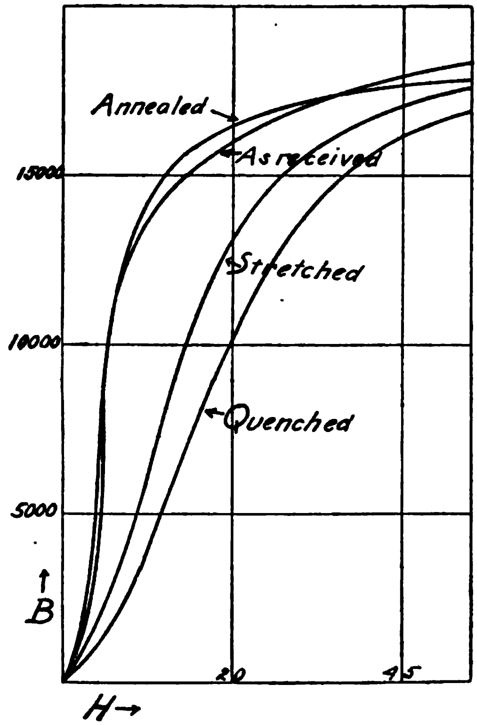


FIG. 10.—*Normal induction of a low carbon steel under different conditions*

There is a certain value of the tension for which the induction is a maximum for a given field. The tension at which the induction is a maximum for a given field decreases with increase in field. In very strong fields this maximum may even disappear, so that the effect of any tension is to diminish the induction. On the other hand, in very weak fields the induction may increase with increase in tension for all stresses within the elastic limit.

All these effects are complicated by the phenomena of hysteresis and the initial changes are different from those that occur after the cycle of changes has been passed through several times.

J. J. Thomson, by a course of dynamical reasoning, has shown that there is a reciprocal relation between the changes in dimensions produced on magnetization and the changes in magnetization produced by mechanical strain. From this theoretical consideration it is possible to foretell one set of phenomena from the data on the other. Both sets of phenomena have been carefully investigated and the reciprocal relation verified experimentally.

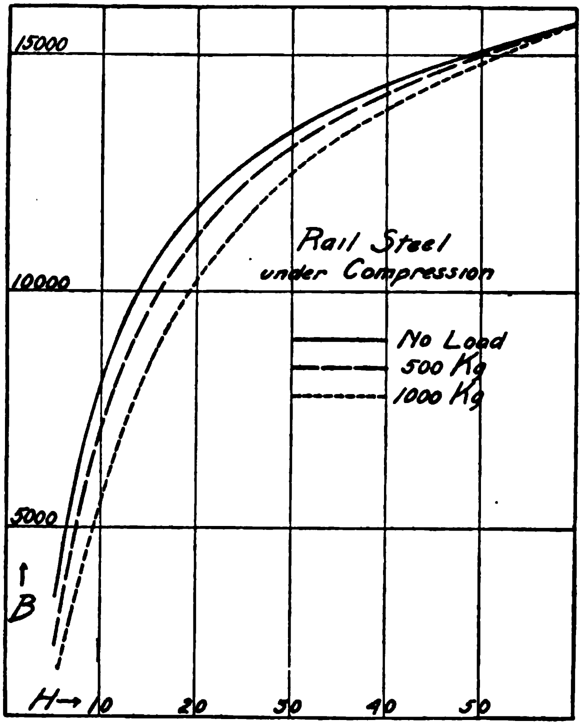


FIG. 11

2. FOR STRESSES BELOW THE ELASTIC LIMIT

Figs. 11 to 16 are taken from an article by Smith and Sherman[5] and illustrate in detail the magnetic changes due to tension and compression.

---

[5] Smith and Sherman, Phys. Rev., N. S., 4, pp. 267–273; 1914.

In this investigation the materials studied were rail steel, mild steel, and silicon steel such as used in transformer plate. Test samples 60 cm long and 1 cm in diameter were subjected to various tensions and compressions and the magnetic induction curves simultaneously determined by the Burrows method.

If a low magnetizing force is applied to a rod under compression with a successively decreasing load, the permeability gradually increases with a steady decrease in this rate of increase as zero load is approached. If tension is applied, the permeability still increases at a diminishing rate until a certain value of load is reached at which the increase ceases. For larger loads the permeability becomes smaller as more tension is applied. The change in rate seems nearly constant and in the same direction throughout.

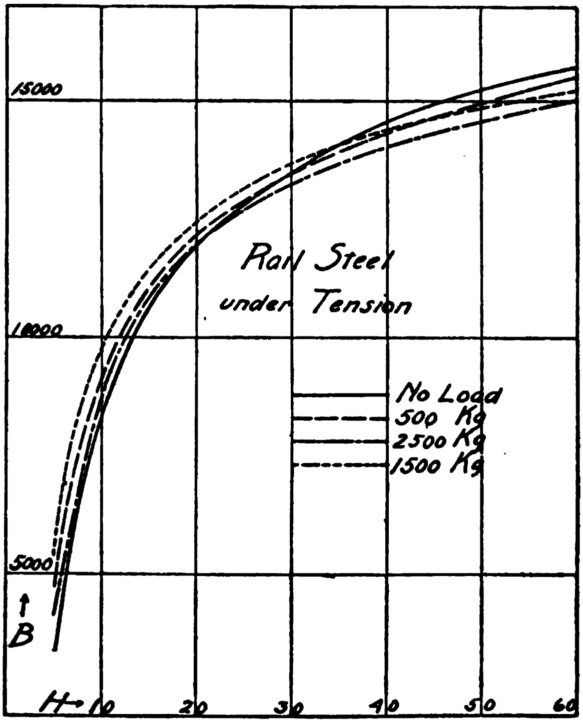


Fig. 12

In all the samples the Villari reversal was found for tension, but not in all cases for compression, although the form of the curve indicated that at higher inductions the reversal might be expected for compression also. The effect of compression was to decrease the permeability at low values of H and to increase it at high values of H, but in much greater degree than the corresponding changes due to tension. The stresses ranged from a tension of 2500 kg per square centimeter to a compression of 1000 kg per square centimeter.

Magnetizing forces from 30 to 55 gausses were used. The greatest change in permeability was found in wrought iron, which showed at a magnetizing force of 15 a decrease from 14 200 gausses to 8600 gausses under a compression of 1000 kg per square centimeter.

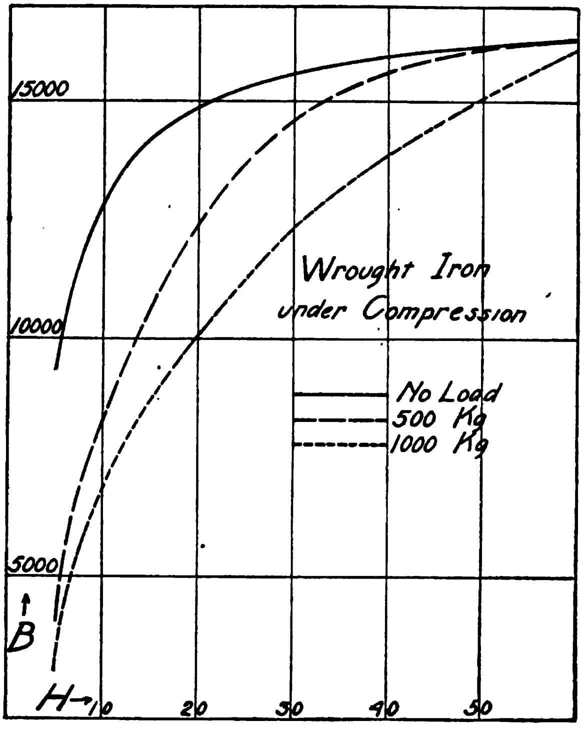


FIG. 13

The complicated manner in which the magnetic induction varies with the tension for different magnetizing forces is brought out in Figs. 17, 18, and 19.[6] Fig. 17 shows that for moderate values of the magnetizing force the induction is always increased by the application of a small tensile load and decreased by a large load. The intermediate load, which produces a maximum induction for the corresponding magnetizing force, is greatest for low magnetizing forces and decreases as the magnetizing force increases, as shown in Fig. 18. The numerical value of the maximum increase produced by tension varies through wide limits, as shown by Fig. 19.

---

[6] Figs. 17–19, 22–25, and 27 are taken, with some modification, from the thesis of Paul D. Merica, "Ueber Beziehungen zwischen den mechanischen und den magnetischen Eigenschaften einigen Metalle bei elastischen und plastischen Formänderungen," Diss. Berlin; 1914.

Fig. 20[7] shows the hysteresis in the magnetic induction when the tension is varied in a cyclic manner. It also shows the difference between the variation of magnetic induction when the load is first applied and that which occurs in succeeding cycles.

Fig. 21 presents in a slightly different form this same magnetic hysteresis after a change in tension. The magnetic effect of any mechanical stress depends not only upon the existing stress but also upon the previous stresses which have been impressed upon the specimen. Work done by the author tends to show that this aftereffect of a given load is reduced, if not completely obliterated, with the lapse of time. Merica shows that if the elastic limit has not been passed the magnetic effect of any stress may be wiped out by demagnetization.

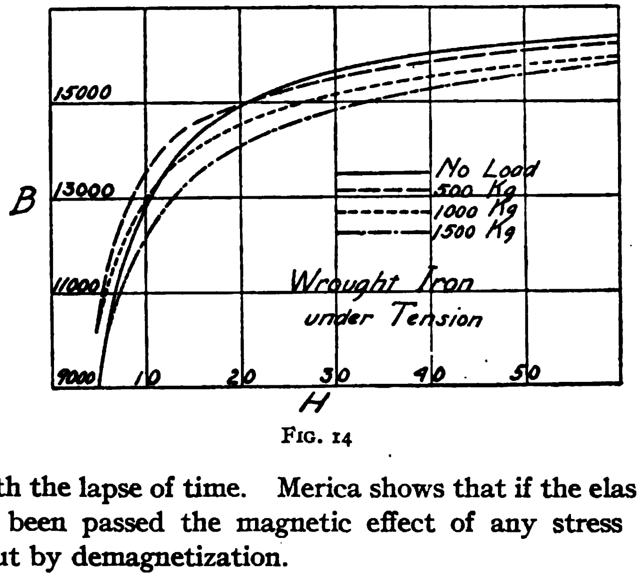


FIG. 14

In the experiment, the results of which are shown in Fig. 22, the test piece was strained beyond the elastic limit. At several stages the load was held constant while the bar was demagnetized and its induction determined. The hysteresis in both the magnetic and mechanical properties is worthy of note. For stresses within the elastic limit neither mechanical nor magnetic curve shows any hysteresis. We must not confuse the procedure of this experiment with that of Fig. 20, in which the magnetizing force was applied continuously without intermediate demagnetization.

---

[7] Figs. 20, 21, and 26 are taken, with some modification, from Ewing, "Magnetic induction in iron and other metals."

3. FOR STRESSES GREATER THAN THE ELASTIC LIMIT

The magnetic behavior of a bar under tension is altered by stressing beyond the elastic limit. The influence of stretching is shown in Fig. 23, where it is evident that both the contour and magnitudes of the curves are changed. Fig. 24 shows how the tension required to give the maximum induction for a given magnetizing force varies with the elastic limits which have resulted from previous stretching. The curve for the upper magnetizing force is so nearly a straight line that it is possible to determine intermediate elastic limits from the magnetic data.

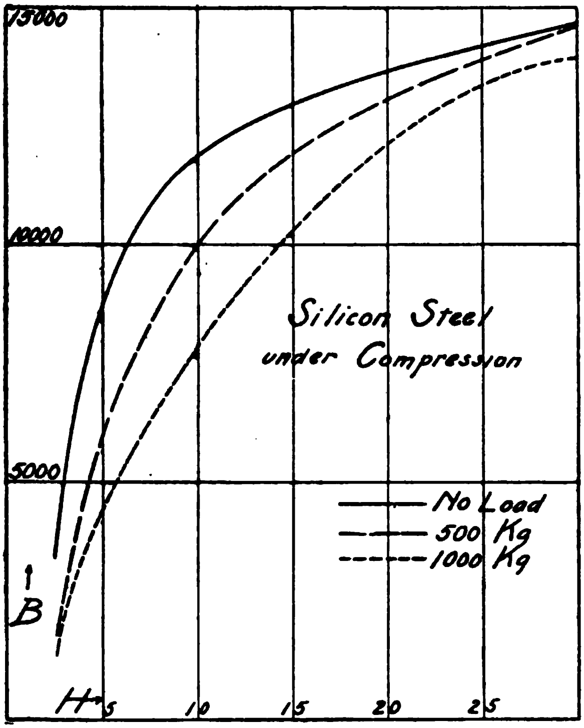


FIG. 15

Fig. 25 shows the manner in which the magnetic flux decreases during the elongation of the bar. The decrease in flux is not proportional to the elongation, so that it is evident that there is some change other than a decrease in cross section taking place within the bar. It is further evident that the greater part of this structural change takes place during the initial elongations.

The magnetic properties of all magnetic materials are modified under tension, though not all in the same manner. Nickel, for instance, shows an increased magnetic induction under compression and a decreased induction under tension, while iron shows the reverse. Fig. 26 gives some idea of the magnitude of these magnetic changes in nickel.

Fig. 27 shows the variation in induction with increase of tension for a sample of nickel steel. The change in induction as the tension reaches the elastic limit is very marked, both in the annealed and the stretched condition.

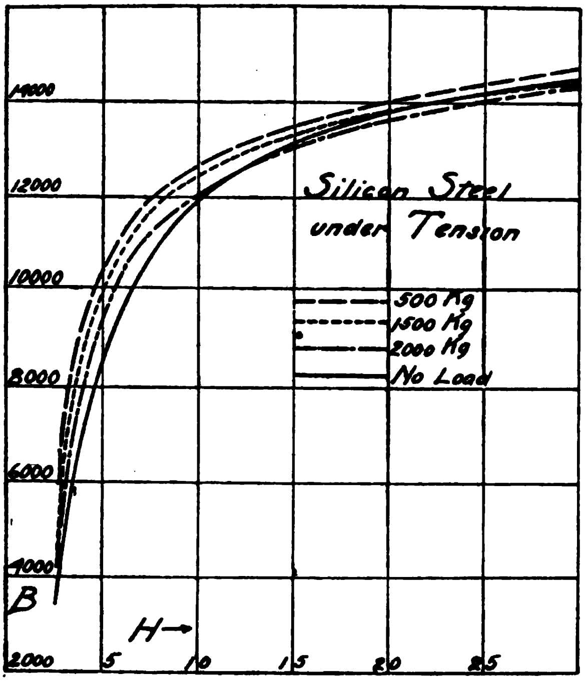


FIG. 16

A general view of the effect that tension below the elastic limit will have on a given material is obtained by a consideration of the curves of magnetostriction,[8] Fig. 28. If a material shows elongation for a given field, it also shows increased induction under tension, and vice versa, for the same field.

(*a*) **Experiments of Fraichet.**[9]—*Method.*—The bar under test is placed in a tensile testing machine and the jaws separated at a constant velocity. A solenoid which surrounds the test bar carries the magnetizing current. A small test coil also surrounding the test specimen is connected to a suitable galvanometer. This test coil is linked with the flux in the bar under tension and any change in this flux gives rise to a corresponding emf which is indicated by the deflection of the galvanometer.

---

[8] S. R. Williams, Phys. Rev., **34**, p. 44; 1912.

[9] L. Fraichet, "Nouvelle méthode d' essai des métaux magnétiques," Ecl. Elc., **36**, pp. 361–369 and 413–422; 1903.

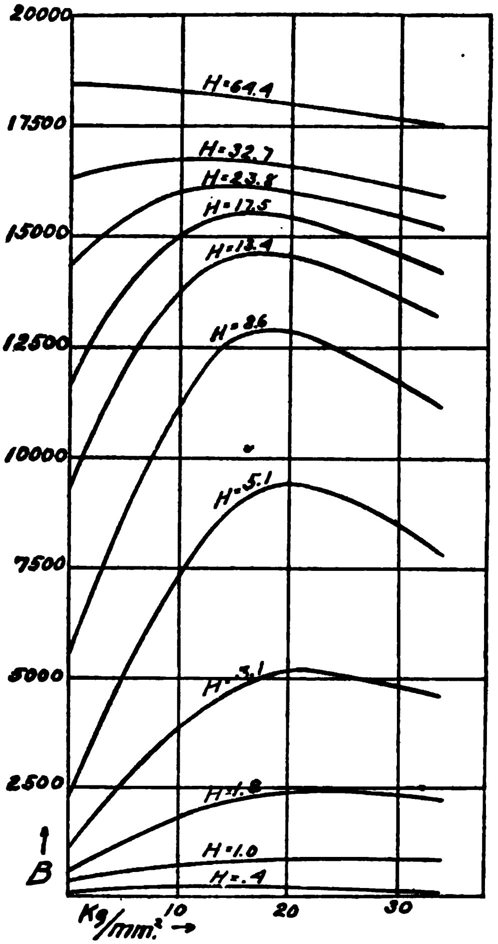


FIG. 17.—*Showing the effect of tension on the magnetization under different field strengths*

Causes of flux variation.—The flux may vary from any or all of three causes: (1) The reluctance of the joints and parts of the magnetic circuit other than the specimen may change; such variations occur when the tension is first applied but die out as soon as the grips of the machine make good contact with the specimen; (2) the reluctance will decrease as the continued ap-

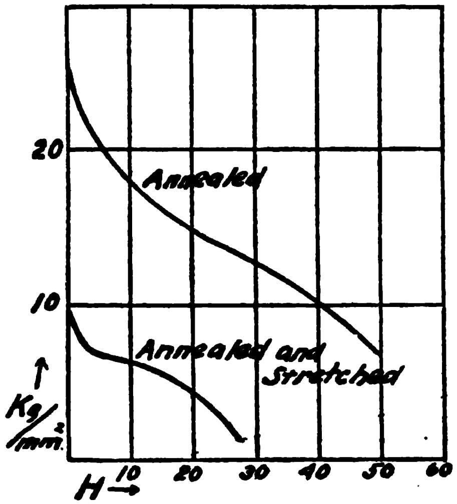


FIG. 18.—*Showing the tension required to produce the maximum induction for a given field*

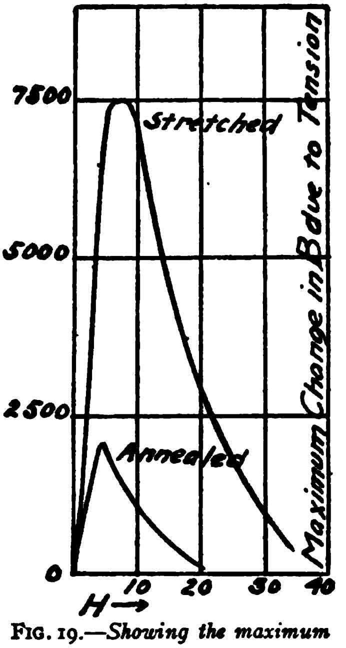


FIG. 19.—*Showing the maximum increase in induction which can be produced by tension*

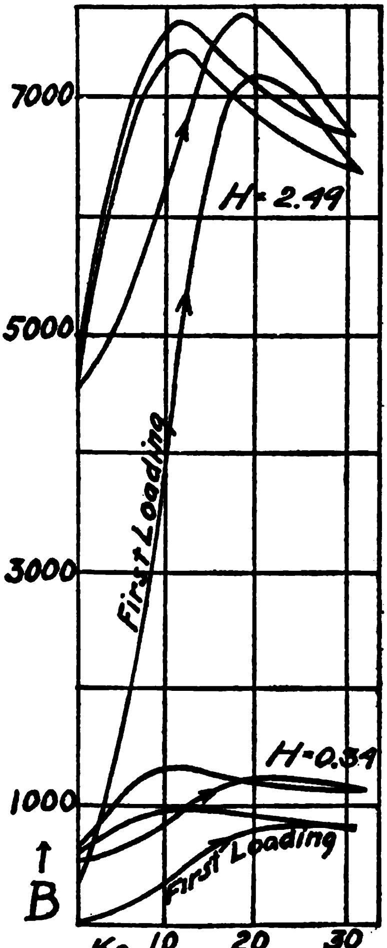


FIG. 20.—*Showing the changes in magnetic induction due to the loading and unloading of a bar under a constant magnetizing force*

plication of tension causes the bar to decrease in cross section; (3) changes in the molecular structure of the metal due to the cold working will probably cause changes in reluctance. Changes in the cross section will be manifested by gradual changes in reluctance, while changes in the structure will take place more or less suddenly.

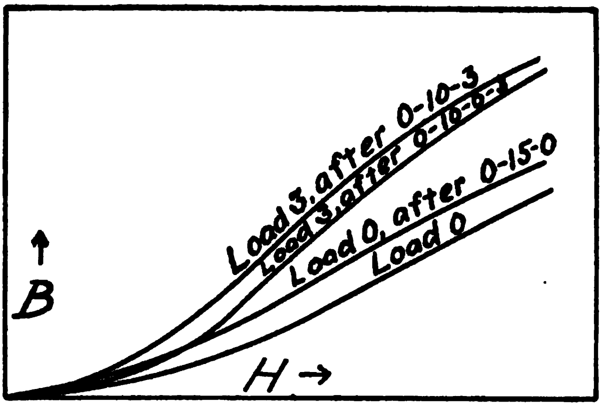


FIG. 21.—*Showing the effect on the magnetic induction due to loads which have been applied and removed before the magnetizing force is applied*

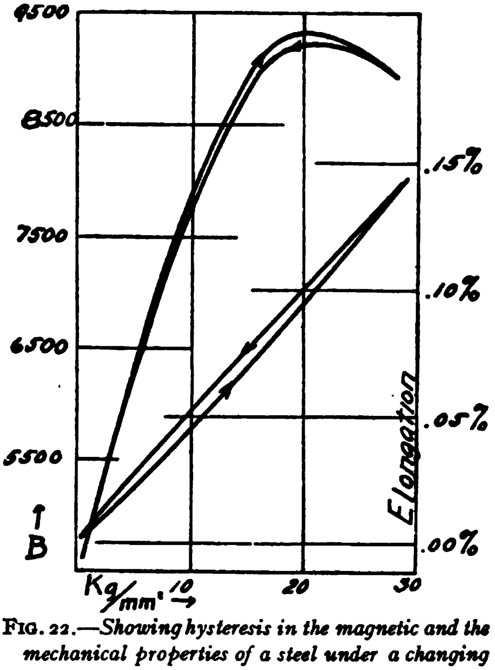


FIG. 22.—*Showing hysteresis in the magnetic and the mechanical properties of a steel under a changing tensile force whose maximum exceeds the elastic limit*

In Fig. 29 the variation of magnetic flux is plotted against the time since the tension machine was started. Curve *II*, which may be taken as a typical curve of this type, shows several well-defined regions. The initial deflection of the galvanometer is positive and may be accounted for by improvement in joint contacts and the well-known increase in permeability due to tension. This region is of no particular importance in the present series of experiments and may exhibit many apparent irregularities. The second region is one indicating a decreasing flux and ends with the point of maximum rate of decrease. This point corresponds to the limit of proportionality between stress and strain. This is the true elastic limit which we may define as the maximum load whose momentary application produces no

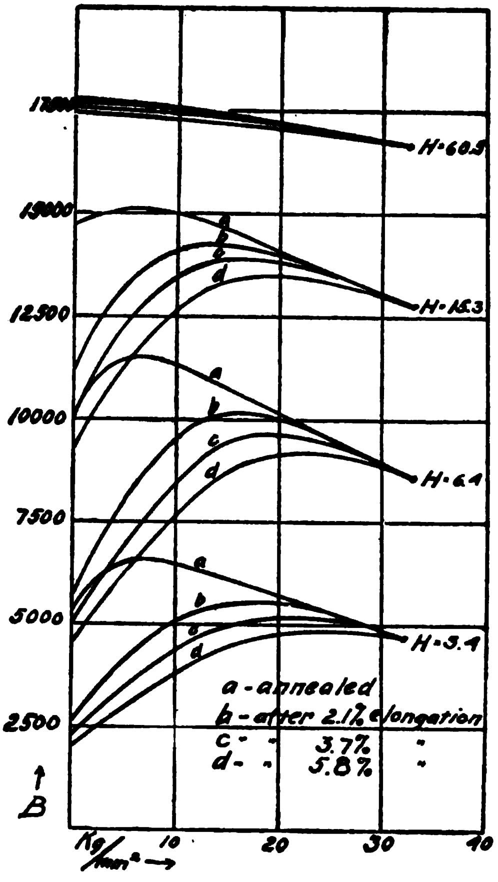


FIG. 23.—*Showing now the effect of tension on the magnetic properties is modified by cold working*

marked modification in dimensions of the bar nor in physical or chemical properties of the metal

The third region is one of more or less violent vibrations of the galvanometer. These magnetic disturbances begin at the yield point of the metal, which is spoken of as the "apparent elastic limit." The fourth, or plastic region, is one of gradual decreasing galvanometer deflections terminated by a sudden but slight drop at the commencement of stricture. The last region shows a rapidly increasing reluctance, and terminates at rupture.

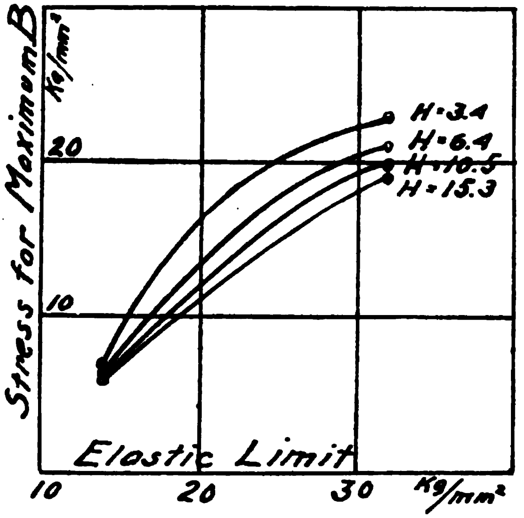


Fig. 24.—*Showing how the elastic limit of a series of cold-worked steels varies with the stress required to give maximum induction for a given field*

The other curves of Fig. 29 show that the nature of these main characteristics is not altered by the value of the magnetizing current employed. Fig. 30 shows the change in tension with time.

If in the initial bar the hardness of the volume elements varies continuously from one part of the bar to another, the molecular transformation of the same elements takes place in a continuous manner. This is what we observe in a quenched bar. The structure of the metal varies continuously. The galvanometer deflection at first increases, passes through a maximum corresponding to the true elastic limit, and finally decreases with a regularity dependent upon the initial homogeneity.

If the distribution of hardness is discontinuous the molecular transformation of the bar will be equally discontinuous, as indicated by the variations in the galvanometer deflections after the limit of true elasticity is reached. We observe these phenomena in bars of soft iron or annealed steel. An annealed bar is therefore composed of elements of varying hardness. Cold working reduces the number of these groups, and consequently produces an elevation of the true elastic limit. Quenching gives the same hardness to all those elements situated on the same concentric layer. A quenched bar is therefore composed of layers having a hardness decreasing from the outside inward.

When the hardest elements have been transformed by the cold working, the flux varies only as a result of change in dimensions. The elements glide one over the other. The specific load corresponding to the commencement of the plastic period is easily measured, and in the opinion of Fraichet may characterize completely the material.

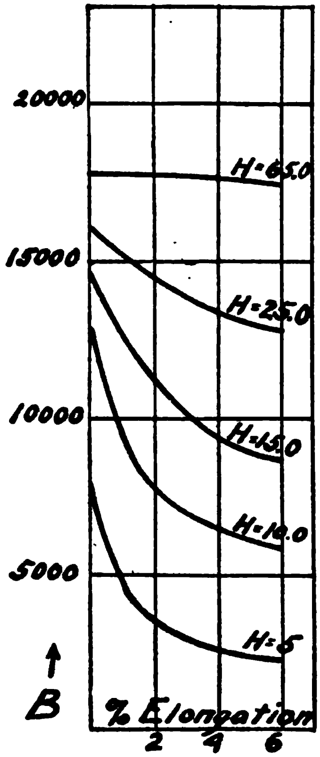


FIG. 25.—*Showing the decrease in magnetic induction corresponding to a given magnetizing force when the test specimen is stretched beyond the elastic limit*

Cold working acts on all the elements of volume and renders the bar homogeneous, and consequently the true elastic limit approaches the plastic load, which, in turn, approaches the ultimate. The effect of cold working is shown in Fig. 31. On the first loading we pass the true elastic limit below 4800 and at 4800 the metal is yielding. When the load is removed and reapplied the true elastic limit is raised to 4800 and the yield point is about 4850. Re-

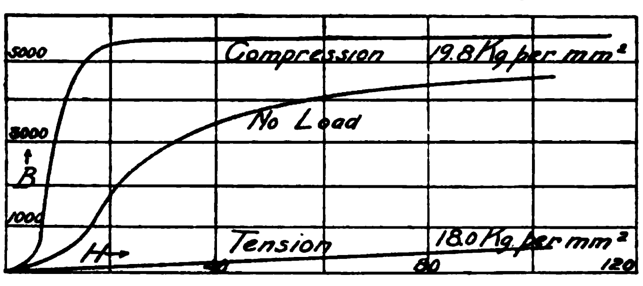


FIG. 26.—*Showing how the magnetization curve of nickel changes under tension and under compression*

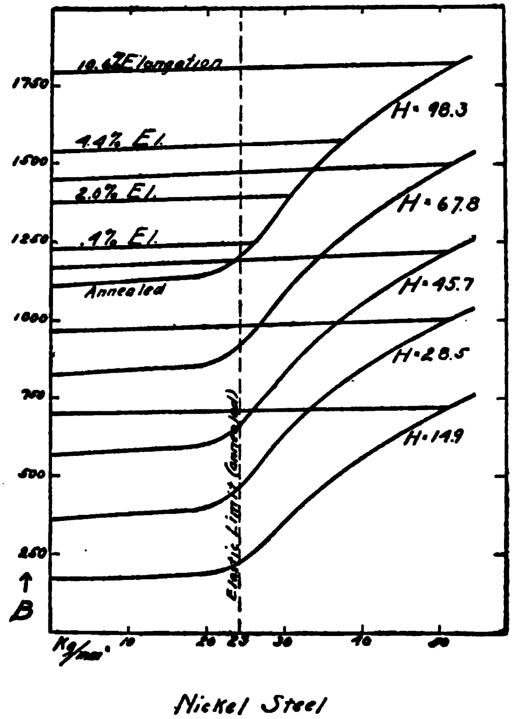


FIG. 27.—*Showing the variation of magnetic induction with tension for nickel steel*

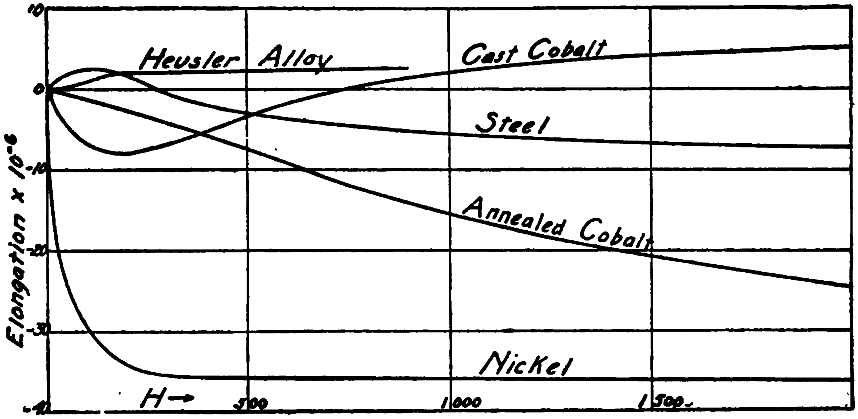


FIG. 28.—*Magnetostriction curves*

moving the load again and reapplying it results in a true elastic limit of 4850, followed immediately by the plastic yield and final rupture. In other words, the bar is homogeneous.

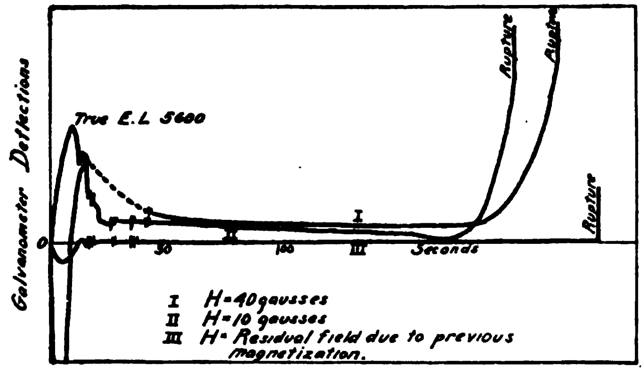


Fig. 29.—*Showing magnetic changes in a bar loaded to the point of rupture*

Fig. 32 shows characteristic magnetic curves for test bars of the same composition, but of different heat treatments.

The true elastic limit is easily determined by this magnetic method, and corresponds to a critical point of molecular equilibrium. The apparent elastic limit or yield point is a function of the previous working of the metal, and consequently does not characterize the metal. The nature of the material is best indicated by the specific plastic load.

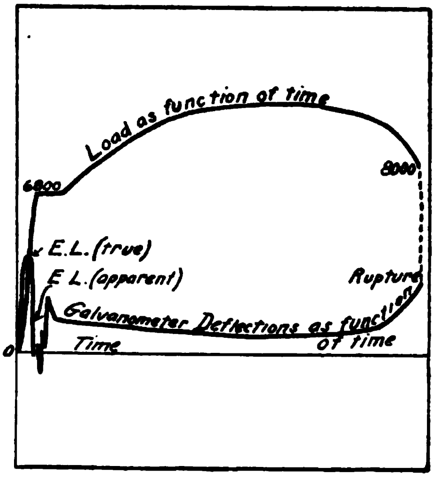


Fig. 30.—*Showing the changes in tension and in the magnetic properties when the tensile machine motor is driven uniformly*

Fraichet[10], elsewhere in a paper on "Sudden variations in reluctance of a magnetized steel bar submitted to fracture as related to Lüder's lines," notes the appearance of lines on the surface of a test bar of steel under a tensile force which correspond exactly with a sudden variation in the magnetic reluctance of the bar. It seems highly probable that the same cause gives

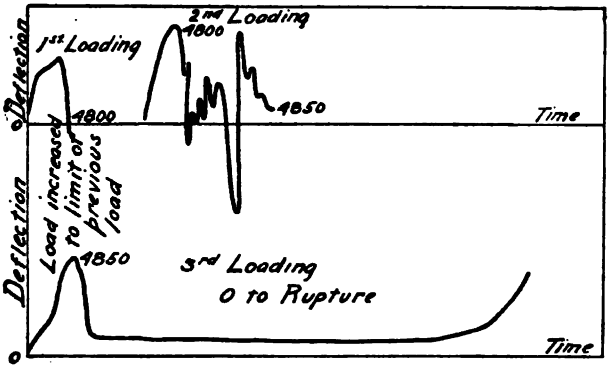


FIG. 31.—*Showing how the cold working of successive loadings beyond the elastic limit changes the magnetic and mechanical properties*

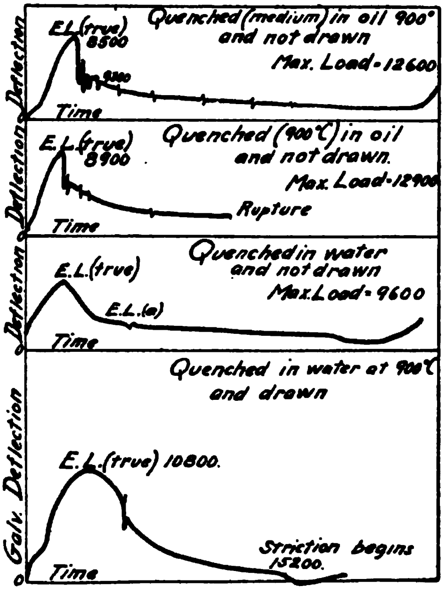


FIG. 32.—*Showing how the magnetic changes in a bar subjected to tension up to the point of rupture depend upon the previous heat treatment*

rise to both these phenomena. Whenever the formation of fresh lines is observed the variation in reluctance is discontinuous, while no new lines are formed as long as the variation in reluctance is not abrupt.

---

[10] Fraichet: C. R., 188, pp. 355–356; 1904.

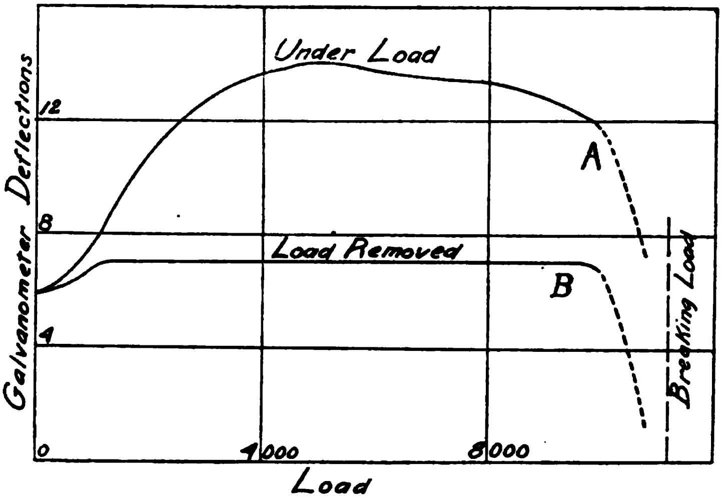


FIG. 33.—*Showing the magnetic induction under load and after the removal of load*

In Fig. 33 curve *A* shows the variations in magnetic induction of a bar of machinery steel under various loads in tension. The induction increases with initial load up to a maximum and then

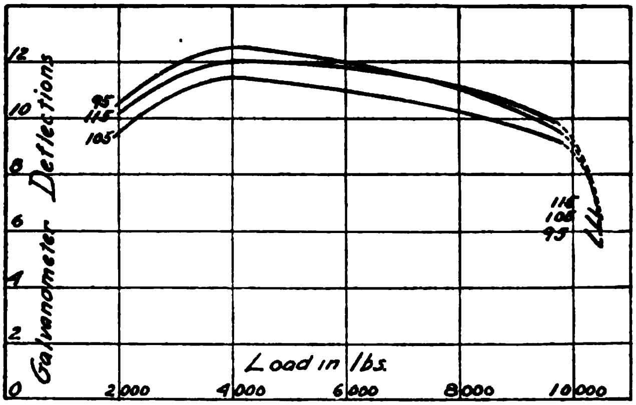


FIG. 34.—*Showing the variations in induction for different parts of a bar during tension*

decreases. At a load which corresponds roughly to the elastic limit the induction decreases abruptly. Curve *B* shows the inductions obtained after the loads indicated by the abscissæ have been applied and removed. This curve is almost a straight line throughout the greater part of its length and falls off abruptly as the elastic limit is reached.

Fig. 34 shows curves of induction under load in which the variation in the induction over three sections of the bar 10 cm apart were determined. The break occurred over the section 95, which, although it had the greatest induction for initial loads, showed the lowest induction at loads approximately the breaking strength. As the material began to yield, the load was decreased slightly, with a corresponding rise of induction as shown. If we assume that initially the greater part of the material at section 95 was under some internal tensile strain, we have at once the explanation of the higher initial induction and the lower final induction, together with the rupture at this section.

IV. INHOMOGENEITIES AND FLAWS

When a bar of steel is placed in a magnetic field the magnitude of the induction and other magnetic phenomena is determined by the nature and amount of material present. From this it follows that if a magnetic exploration is made along the length of a bar, magnetic variations may be expected in nonhomogeneous material. The following experiments bear this out.

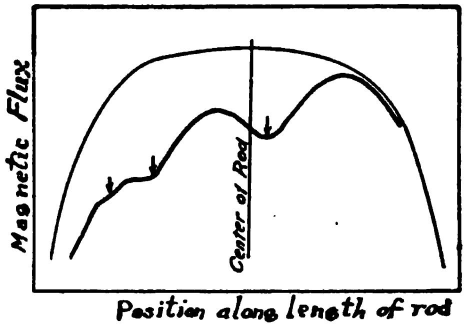


FIG. 35.—*Showing irregularities in distribution of flux in a rod which has been rendered nonhomogeneous by stamping numbers as indicated by the arrows*

In Fig. 35[11] is shown the variations in magnetic induction in a bar which forms one side of a rectangular magnetic circuit and is magnetized by a surrounding solenoid. The upper curve shows the normal variation of flux in a bar which is approximately uniform. The lower curve shows the variation of flux in the same bar after a single number has been stamped on the bar at each of the points indicated by the arrows. The magnetic changes produced by the stampings are evidenced by a decided reduction in the induction at these points.

---

[11] Burrows, Bull. Bureau of Standards, 6, p. 62, 1909 (Reprint No. 117).

Fig. 36[12] shows the variation in permeability along the lengths of each of two bars both before they have been distorted (dotted lines) and after they have been bent through a given angle and then restraightened (solid lines). After this last operation each bar was broken in a tensile testing machine. The permeability shows a remarkable change due to the bending. In the immediate neighborhood of the bend there is a region of increased permeability and close to it a region of decreased permeability. In each case the rod broke in the region of maximum permeability. In this connection we may refer back to Fig. 34, where, it was noted, the break occurred over the section which had initially a maximum permeability.

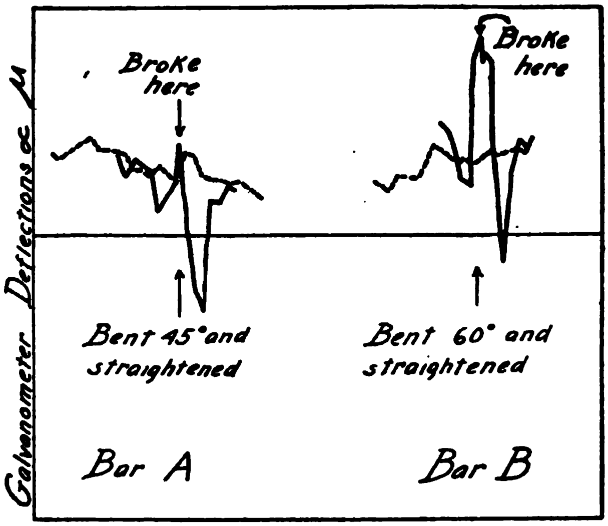


FIG. 36.—*Flux distribution of a bar before and after bending and restraightening*

The magnetic homogeneity of a bar may be investigated in terms of the flux distribution when placed in a magnetic field. With a single stationary coil one may measure the total flux. With two opposing stationary coils the magnetic leakage may be measured. With two opposing and movable test coils the variation in leakage may be measured. Mr. Sanford, of the magnetic section of the Bureau of Standards, has perfected the details of this last method of examination and the author is indebted to him for the following curves showing certain characteristic conditions.

---

[12] Figs. 34 and 36 are taken from a paper by the author presented before the American Physical Society, April, 1912.

In Fig. 37 are plotted the observations on seven bars which were originally homogeneous as shown by a preliminary examination and were later rendered inhomogeneous in the manner indicated. Curve *A* is the record of a uniform rod and is similar to the records of the other rods before modification. The criterion of a uniform rod is an approximately straight line. An upward projection indicates a magnetically hard spot and a downward projection indicates a soft spot. The sharp upward projection of *B* is due to a saw slot 3 mm deep in a rod of 12.7 mm diameter. Rod *C* was bent

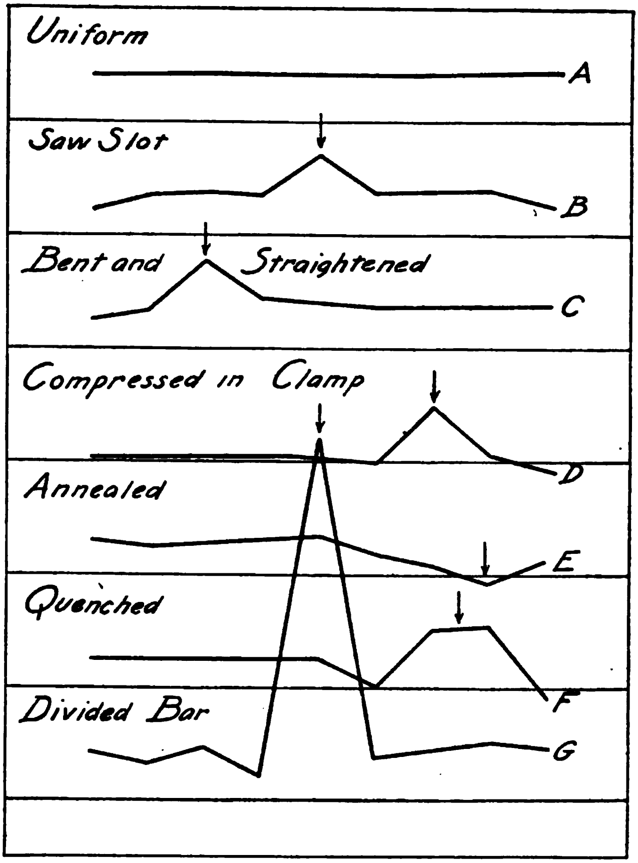


Fig. 37.—*Mechanical inhomogeneities as shown by variations in the rate of change of leakage*

through an angle of 10° and straightened, while *D* was repeatedly compressed between the jaws of a small clamp operated by a thumbscrew. In each of the cases the magnetic inhomogeneity is similar to that caused by the saw slot. In *C* the bar was heated by a small flame and cooled in air. The resulting softness is apparent from the downward projection of the curve. *F* was heated over a greater length and quenched. The resultant hardness extends over a greater length, as might be expected. *G* is a bar which was cut in half and put together with a threaded joint and carefully finished surfaces, so that it presented the appearance of a continuous bar. The projection due to this treatment is striking.

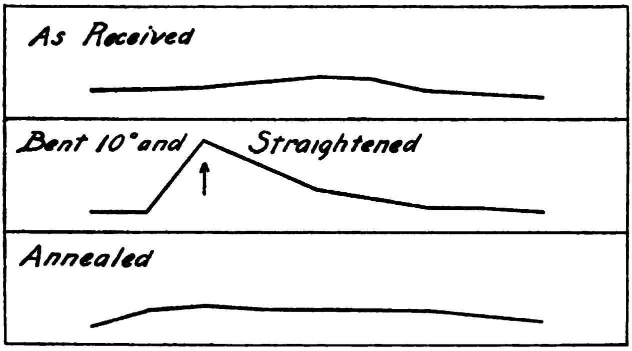


Fig. 38.—*Showing the effect of bending and restraightening and of annealing on the magnetic homogeneity along the length of a bar*

In Fig. 38 records are made of a bar as received, after bending and restraightening, and after annealing. It is to be noted that the cold bending produces a marked inhomogeneity which is entirely removed by subsequent annealing.

Such tests as these which indicate the presence of mechanical strains, coupled with the fact that such strains may be relieved by heating to a temperature below which structural changes occur, open up a wide field of possible applications.

1. INHOMOGENEITIES IN STEEL RAILS

At the present time the author is carrying on an investigation of the magnetic inhomogeneities along the length of steel rails.

The rail to be examined and a similar rail are placed side by side. The rail under test is surrounded by a narrow test coil which is in electrical connection with a galvanometer. Surrounding the rail for some distance on each side of the test coil are two magnetizing solenoids. Opposite these two solenoids and surrounding the auxiliary rail are two similar solenoids. The test coil and solenoids are rigidly connected together and mounted on a carriage which is free to travel along the test rail and its companion rail. Fig. 39 is a photograph of a pair of rails with the coils in place. Underneath the carriage is shown the electric motor which drives the apparatus along the length of the rails.

Any change in the magnetic induction in the test rails manifests itself by a deflection of the galvanometer coil. The position of the galvanometer coil is recorded by means of a spot of light reflected onto a photographic film. In order to make a continuous record the film is driven at a uniform rate by an electric motor. The galvanometer and recording apparatus are shown in Fig. 40. A great many modifications of the method of exploration were made. Some of the records, for example, were taken with one test coil surrounding each rail and coupled so that the emfs generated opposed each other.

To explore the length of a rail the current in the magnetizing solenoid is adjusted and the electric motors driving the carriage and the film started simultaneously.

In this preliminary work in order to get some idea of the importance of the magnetic irregularities observed several artificial defects were made in some ordinary 100-pound rails which happened to be available. These rails had all been in service and had been submitted to the bureau because of suspected imperfections. In general, they are from the same heat as other rails which have caused wrecks or otherwise failed in service.

In order to simulate the effect of a transverse fissure a saw slot 1 mm wide cutting away about 10 per cent of the section of the rail was made. This slot was filled in with high permeability transformer iron and the surface thus filled in was smoothed down with a file.

Fig. 41 shows the magnetic effect of the saw slot very clearly. In a later test of this same saw slot without the soft iron filling the galvanometer deflection was so violent that the spot of light went far beyond the bounds of the film. In either case the magnetic test shows the position of the slot within 1 cm. On another rail a similar slot was cut into the base and gave a record of similar characteristics.

To determine whether this method would detect a flaw in the web of a rail, records of the magnetic condition were made with holes drilled in the web. The effects of holes of various sizes are

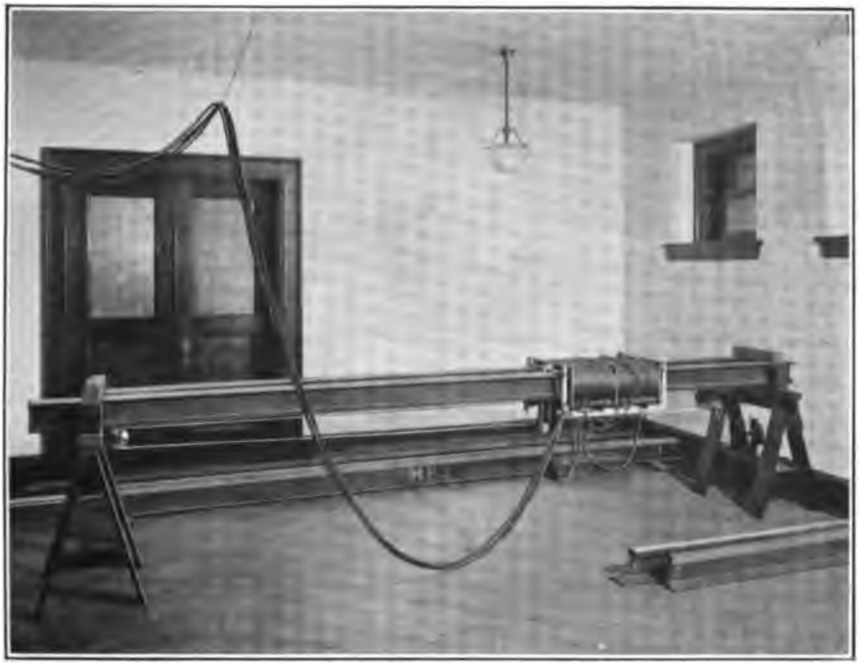


FIG. 39.—*Photograph of rail-exploring apparatus*

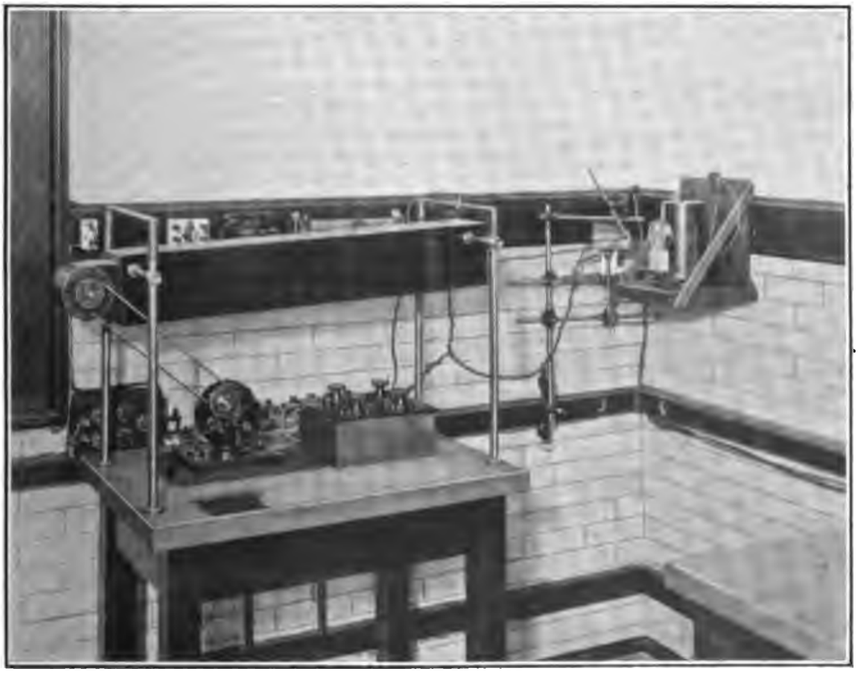


FIG. 40.—*Photograph of recording apparatus used in the exploration of rails*

shown in Fig. 41. It is quite evident that such a defect does make itself known by the magnetic exploration, and that the magnetic importance is proportional to the size of the hole.

In addition to the effects of the saw slot in the head and the holed drilled in the web, several other observations may be made on Fig. 40. The fact that the records are not all of the same length is due to slightly different rates of travel of the car in the various cases. The breaks in the curves are caused by shading the recording light beam at intervals corresponding to a carriage travel of 50 cm. The consistency with which the magnetic record repeats itself is quite evident from an examination. All the principal characteristics and most of the minor details of one curve are reproduced in the other two. The marked magnetic inhomogeneity noticed at the left of these records is due to some

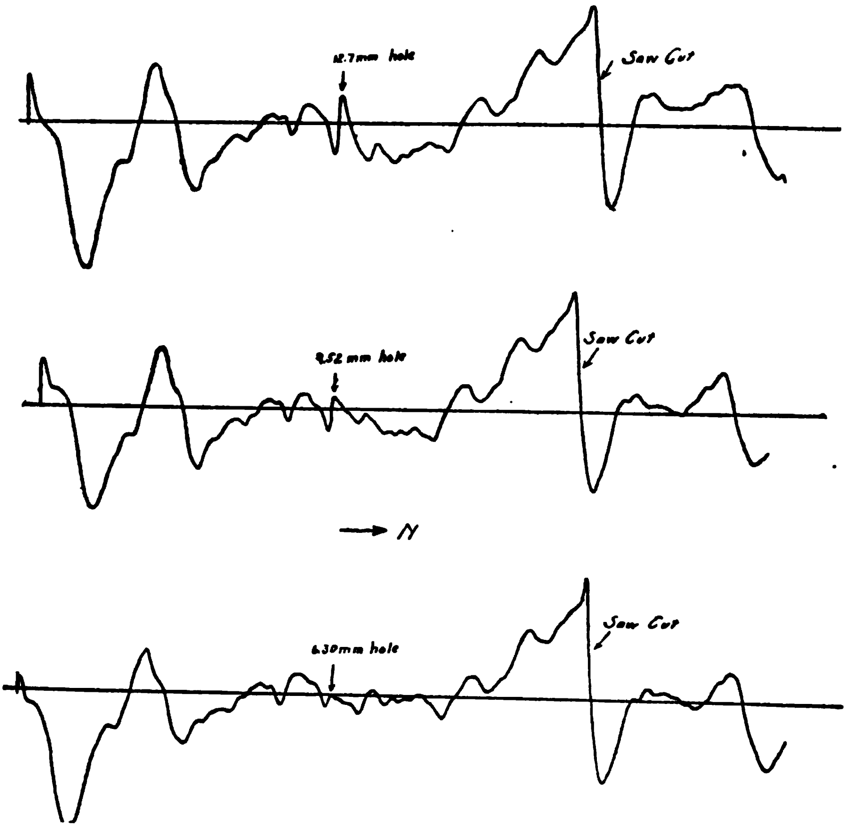


FIG. 41.—*Photographic record of inhomogeneities in a standard steel rail after service, showing the effect of artificial flaws*

unknown characteristic of this region of the rail which, as yet, we have not had time to investigate.

In Fig. 42 of another rail the record shows a wavy form of remarkable uniformity. It appears from a comparison of the magnetic record with the tie marks on the rail that there is a cycle of magnetic variation which repeats itself at distances equal to the spaces between ties. The portion of the rail over the tie is magnetically harder than the intermediate portions. This is of considerable interest because of the fact that rail failures occur more frequently over the ties than in the interspaces. The irregularity in the middle of the curve is worthy of comment. At the point *A* the curve shows a relative hardening instead of the maximum of magnetic softness that might be expected. The rail head was carefully examined in this region and was found to have imbedded in it a number of nodules of a metal of finer texture and greater hardness. It has been suggested that these may be small fragments from the rolls.

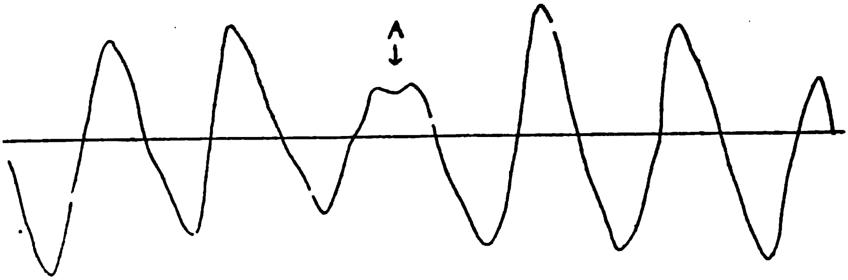


Fig. 42.—*Photographic record of a standard steel rail after service, showing the effect of tie strains and local hard spots*

Quite an ingenious application of the fact that mechanical inhomogeneities are accompanied by corresponding magnetic variations was made by McCann and Colson[13] in 1908.

The apparatus consists essentially of a solenoid surrounding the mine hoist cable to be tested and connected in series with a suitable current source and measuring instrument. Any variation in the magnetic constants of the cable, due either to the breaking of individual strands or hardening caused by excessive strains, is indicated as soon as the defective portion passes through the apparatus. Suitable recording apparatus is provided so that a test of the entire cable is made every time the car travels the length of the shaft.

---

[13] Western Electrician, 43, pp. 76–77; 1908.

V. CONCLUSIONS

The experimental evidence, of which only a small portion has been presented in this paper, seems to point to the conclusion that there is one and only one set of mechanical characteristics corresponding to a given set of magnetic characteristics, and conversely there is one and only one set of magnetic characteristics corresponding to a given set of mechanical characteristics.

Although there is no evidence to refute the preceding rather broad statement, the utility of this generalization is decidedly limited by the complexity of the relations due to the large number of variables and the lack of sufficient quantitative data. Quantitative data, however, are gradually being obtained by the author and others who are working on this problem. The application of the magnetic tests is further limited by practical difficulties in testing irregular shapes. Even with these limitations, magnetic testing in conjunction with mechanical testing may be expected to be of considerable value in determining mechanical properties.

It has been shown that magnetic observations taken during the course of a tensile test indicate the time when the true elastic limit, the yield point, the necking down point, and the ultimate strength are reached. In addition, the magnetic data give some idea of the uniformity of the material.

If it is once determined what treatment is requisite for a given steel, a magnetic test may be used to determine whether or not the material has been brought into the desired condition.

It is quite possible that the magnetic data may be used to define a bar of steel. In no other manner than by a magnetic examination is it possible without doing violence to the specimens to determine whether two steel bars are identical in properties.

A determination of the magnetic uniformity of a piece of steel may be used as an index of the mechanical homogeneity.

A magnetic test indicates the character of the entire cross section of the metal, rather than merely a surface phenomenon, as in the case of certain hardness tests.

Notwithstanding the possibilities of the magnetic test, it must be remembered that at present they are possibilities only. Before the magnetic characteristics can be of much practical importance a great deal of investigation is necessary and a large number of accurate measurements on specimens of known chemical composition and heat treatment must be made.

Before a magnetic test can be of service as an indicator of the mechanical characteristics in any particular case, preliminary work must be done to determine the most suitable magnetic data and also the minimum amount which will give the desired information. Among the magnetic characteristics which may be used are permeability, residual induction, coercive force, hysteresis energy, etc., and each of these may be taken in connection with any one of a great number of magnetizing forces.

For a concrete case, suppose that the problem is to devise a magnetic test for a steel spring or a crank axle. The preliminary investigation would take some such course as the following:

1. Determination of magnetic normal induction curves and hysteresis data for test pieces made of the materials to be tested and submitted to the various heat and mechanical treatments that may be expected in practice.

2. Comparison of the above magnetic data with the corresponding mechanical data and the determination of the most suitable magnetic data to use.

3. Working out of the experimental details so that the required magnetic measurements may be made on the full-size commercial specimen.

4. Checking out of magnetic and mechanical data on the full-size specimens to be sure that the same conditions are fulfilled as in the case of the original test pieces.

Operations 1, 2, and 4 are time consuming, but do not offer any great difficulties that can not be overcome by patient intelligent experimentation. The third operation may offer practical difficulties due to irregularities in the shape of the material to be tested. Relatively long objects uniform in diameter, such as rails, steel rims, band screws, drills, and steel cables, present no difficulty. Relatively long objects whose cross section changes gradually from section to section, such as spring leaves, straight axles, and files, present comparatively little difficulty. Relatively long objects of irregular section, such as crank axles, present great but not insuperable difficulty. Short, thick castings present difficulties which for the present seem insuperable.

WASHINGTON, March 30, 1915.

VI. BIBLIOGRAPHY

The following is a list of references dealing with the correlation of the magnetic with other physical characteristics:

1841. Joule. (Tension.)
1847. Matteuci. Comp. Rend., **24**, p. 301. (Tension.)
1858–1886. Wiedemann. Pogg. Ann., **96**, p. 17, 1858; **103**, p. 566, 1858; **106**, p. 161, 1859; Wied. Ann., **27**, p. 376, 1886; **41**, p. 200, 1886. (Torsion.)
1861. Righi. Beibl, **5**, p. 62, 1881. (Hardness.)
1863. von Waltenhofen. K. Akademie, **48**, 1863. (Hardness.)
1865. Villari. Pogg. Ann., **126**, p. 87. (Tension.)
1874. Ruths. Inaug. Diss.-Darmstadt. (Hardness.)
1875. Thompson. Proc. Roy. Soc. Lon., **23**, pp. 445, 473. (Tension.)
1875. von Waltenhofen. Dingler's Polytec. Jour., **217**, pp. 357–360. (Hardness.)
1876. Fromme. Göttingen Nachrichten, 1876. (Hardness.)
1876. Ruths. Dortmund, 1876. (Hardness.)
1876. Gaugain. Comp. Rend., **82**, p. 144. (Hardness.)
1876. Trève and Durassier. Comp. Rend., **82**, p. 217. (Hardness.)
1877. Thompson. Phil. Trans. Roy. Soc., **166**, Pt. 2, p. 693. (Tension.)
1878. Thompson. Proc. Roy. Soc. Lon., **27**, p. 442.
1878. Gray. Phil. Mag. (5), **6**, p. 321. (Hardness.)
1878. v. Kerpelz. (Chemistry—Hardness.)
1879. Thompson. Phil. Trans. Roy. Soc., **170**, p. 55. (Tension.)
1879. von Waltenhofen. Dingler's Polytech. Jour., **232**, pp. 141–150. (Hardness.)
1879. Thompson. Phil. Trans., **179**, p. 55. (Torsion.)
1879. Hughes. Proc. Roy. Soc. Lon., **32**, pp. 25, 213. (Torsion.)
1881. Pictet. Arch. de Gen. (3), **6**, pp. 113–125. (Mag. hardness.)
1881. Metcalf. Beibl., **5**, p. 895. (Mag. hardness.)
1883. Skida. Proc. Roy. Soc. Lon., **35**, p. 404. (Tension.)
1885. Ewing. Phil. Trans. Roy. Soc. (Tension.)
1885. Barus and Strouhal. Bull. U. S. Geolog. Surv., **14**. (Mag. hardness.)
1888. Ewing. Phil. Trans. Roy. Soc. (Tension.)
1889. Nagaoka. Phil. Mag., **27**. (Torsion.)
1890. Chree. Phil. Trans., **329**, 1890.
1891. Smith. Phil. Mag., **32**, p. 383. (Torsion).
1894. Squier. Electrician, **34**, p. 90, 1894. (Magnetism of gun steel.)
1896. Grösser. Diss. Rostock, 1896. (Torsional magnetostriction.)
1896. Ebeling and Schmidt. Wied. Ann., **58**, pp. 330–341. (Magnetic inhomogeneity.)
1900. Barus. Am. J. Sci., **10**, p. 407. (Torsional magnetostriction.)
1902. Lisell. Diss. Upsala, 1902. (Hydrostatic pressure.)
1903. Fraichet. Ecl. Elec., **36**, pp. 361–369, 413–422. (Tension.)
1904. Fraichet. Comp. Rend., **138**, pp. 355–356. (Tension.)
1904. Frisbie. Phys. Rev., **18**, p. 432. (Hydrostatic pressure.)
1904. Honda and Shimizu. Journ. Sci. Coll., Tokyo, **19**. (Elasticity.)
1904. Gerdien. Ann. de Phys., **14**, p. 51. (Torsion.)
1904. Bidwell. Roy. Soc. Proc., **74**, p. 60. (Effect of annealing on magnetostriction.)

1906. Kann. Phys. Zs., 1906, pp. 526–527. (Inhomogeneities.)
1906. Piola and Tieri. Acad. Lin. Atti., **15**, pp. 231, 566. (Torsion.)
1907. Maurain. Jour. de Phys., **6**, p. 380. (Torsion.)
1907. Bouasse and Berthier. Ann. Chim. Phys., **10**, pp. 199–228. (Torsion.)
1907. Honda and Terada. Phil. Mag., **18**, p. 36, 1907. (Elasticity.)
1907. Honda and Terada. Phil. Mag., **14**, p. 65, 1907. (Stress.)
1907. Williams. Phil. Mag., **18**, p. 635. (Hydrostatic pressure.)
1908. Maurain. Jour. de Phys., **7**, p. 497. (Cyclic tension.)
1908. McCann and Colson. Western Electric, **48**, p. 76. (Inhomogeneities.)
1908. Anonymous. Iron Age, **81**, pp. 1162–1164. (Hardness.)
1908. Wassmuth. Biebl, **82**, p. 901. (Torsion.)
1908. Gumlich and Vollhardt. E. T. Z., **88**, pp. 903–907. (Influence of mechanical working.)
1909. Brown. Roy. Dub. Soc. Pro., **17**, pp. 101–175. (Mechanical influences.)
1909. Brown. Roy. Dub. Soc. Pro., **12**, pp. 101–122, 175–189. (Torsion.)
1909. Burrows. Bull. Bureau of Standards, **6**, pp. 59–62, 1909. (Inhomogeneities.)
1909. Waggoner. Phy. Rev., **28**, pp., 393–404. (Low temperature, carbon content.)
1909. Mars. Stahl und Eisen, **29**, pp. 1673–1678, 1769–1781. (Hardness.)
1909. Pellet. Jour. de Phys., **8**, pp. 110–117. (Torsion.)
1910. Du Prel. Diss. München. (Hydrostatic pressure.)
1910. Encoli. N. Cim., **20**, pp. 317–340. (Tension and torsion.)
1910. Brown. Roy. Dub. Soc. Proc., **12**, pp. 36, 480–497. (Magnetotorsion, elastic limit.)
1911. Goerens. Iron and Steel Inst., **III**, pp. 320–400. (Effect of cold working and annealing.)
1911. Ercoli. N. Cim. (6), **1**, pp. 213–222, 237–268. (Tension and torsion.)
1911. Brown. Roy. Dub. Soc. Proc., **12** (3), pp. 28–48. (Tension in nickel.)
1912. Beckman. Arkiv för Mat. Astrofysik. (Hydrostatic pressure.)
1912. Devries. Proc. I. A. T. M., Sixth Cong. (Tensile strength and hardness.)
1912. Burrows. Proc. I. A. T. M., Sixth Cong. (Report on problem 28, general subject.)
1912. Waggoner. Phy. Rev., **94**, pp. 58–65. (Magnetic and elastic properties of a series of iron carbon alloys.)
1913. Devries. Proc. A. S. T. M. (Hardness, toughness, tensile strength.)
1913. Goerens. Stahl und Eisen, **84**, pp. 282–285. (Magnetic and mechanical properties of mechanically hardened and annealed steel.)
1913. Burrows. Bull. Soc. Auto Engr., Nov., 1913. (General.)
1913. Burrows. Proc. A. S. T. M. (Hardness, toughness, tensile strength.)
1914. Hadfield and Hopkinson. Lon. Eng., **97**, pp. 756–759. (Magnetic and mechanical properties of manganese steel.)
1914. Smith and Sherman. Phys. Rev. N. S., **4**, pp. 267–273. (Tension and compression.)
1914. Merica. Diss. Berlin. (Tension; many valuable data.)
1914. Tafel. Stahl und Eisen, **84**, pp. 574–578. (Tension.) (In drawn bars the B–H curve shows sharp changes near the yield point.)
1914. Mathews. Proc. A. S. T. M., **14**, pp. 50–71. (Hardness.)

For a good bibliography on magnetostriction, see Dorsey, Phy. Rev., **80**, p. 178, 1910.

GENERAL DESIGN OF CRITICALLY DAMPED GALVANOMETERS

By Frank Wenner

CONTENTS

Page
I. Introduction 211
II. Theory 212
  1. The operation constants 212
  2. The intrinsic constants 215
  3. Operation constants in terms of intrinsic constants 216
  4. Relations between operation constants 223
III. General design 223
  1. Number of operation and intrinsic constants 223
  2. Intrinsic constants in terms of operation constants 225
  3. Procedure in the general design 229
  4. Design for current sensitivity 231
  5. Design for voltage sensitivity 235
  6. Design for $\int idt$ sensitivity 238
  7. Design for $\int edt$ sensitivity 240
  8. Detail design 241
IV. Summary 243

I. INTRODUCTION

The theory of the galvanometer, when used under the critically damped condition as a detector of constant voltage in a circuit of fairly low resistance, is given in papers by White[1] and Jaeger[2], published about 10 years ago. In these papers some of the equations which we shall use are given. However, we wish to consider sensitivities to current and voltage impulses as well as to steady current and voltage, and in order that the matter may be presented as a unit, the theory, in so far as it is needed in the design of such galvanometers, will be given here. That is, we shall show the relations between those constants of a galvanometer with which the user is concerned and those constants with which the maker is concerned.

---

[1] Physical Review, **19**, p. 305; 1904.

[2] Zeitschrift für Instrumentenkunde, **23**, p. 261 and p. 353, 1903; and Annalen der Physik, **326**, p. 64, 1906.

The user is concerned with the period, the resistance which must be put in series or parallel in order to give critical damping, and the sensitivity to the quantity the galvanometer is used to detect or measure. These will be referred to as the operation constants. The maker is concerned with the inertia constant, the damping constant, the restoring constant, the dynamic constant, and the resistance—constants which depend upon the kind of material used, the number of turns, the intensity of magnetization, and the size and the proportions of the parts of the galvanometer. These will be referred to as the intrinsic or construction constants. These two sets of constants are necessarily interdependent, and a knowledge of the relations existing between them is necessary for an understanding of the subject of galvanometer design. We shall, therefore, show in what manner each of the operation constants depends upon the intrinsic constants.

These relations will then be used in establishing a procedure for finding a set or sets of values for the intrinsic or construction constants, such as will give previously selected or specified values for those of the operation constants which pertain to the class of work in which the galvanometer is to be used. The finding of some set of values for the intrinsic constants which may be realized in the construction without unnecessary difficulty, and which will give the specified values for the operation constants, constitutes what we call the general design of a galvanometer. The matter will be considered primarily from the standpoint of the design of moving coil galvanometers of high sensitivity, though much of the discussion will apply equally well to the less sensitive galvanometers with pointers and to galvanometers of the moving magnet type. The way in which particular values for the intrinsic constants may be realized, and other matters pertaining to what we call the detail design, can not be considered in this paper.

II. THEORY

1. THE OPERATION CONSTANTS

Galvanometers are used critically damped in four distinct classes of measurements, in each of which the quantity to be detected or measured is different.

In the first (which we shall refer to as class A) it is the current, or change in the current, in a circuit including the galvanometer. The measurement of insulation resistance by the direct deflection method using a fairly high voltage is an example of this class of measurements. Here the sensitivity which should be considered is to current.

In the second (or class B) it is the change in the voltage in the circuit in which the galvanometer is connected which is to be detected or measured. The change in voltage in the galvanometer circuit, on reversing the test current through a bridge which is not exactly balanced, is an example of this class of measurements. Here the sensitivity which should be considered is to voltage.[3]

In the third (or class C) it is the quantity of electricity suddenly passed through the circuit, including the galvanometer, which is to be detected or measured. The comparison of the capacities of condensers by the ballistic throws given, when they are charged to the same voltage and discharged through the same galvanometer, and the comparison of capacities by the method of mixtures, are examples of this class of measurements. Here the sensitivity which should be considered is to impulsive rush of a quantity of electricity $q=\int idt$ through the circuit including the galvanometer.

In the fourth (or class D) it is the time integral of the electromotive force in the circuit. Examples of this class of measurements are the comparison of magnetic fields by the ballistic throws they give, when a coil connected in series with the galvanometer is suddenly removed first from one field and then from the other, or the comparison of two mutual inductances by connecting their secondaries differentially in series with the galvanometer and simultaneously reversing the currents in their primaries, adjusting the ratio of the currents so as to make the ballistic throw zero. Here the sensitivity which should be considered is to the $\int edt$, where e (the voltage) is negligibly small except for a very short time.

Besides the sensitivity to the quantity to be detected or measured the user of a galvanometer is concerned with the time between the change which causes the deflection and the instant when the deflection may be considered to have reached a constant value; or, in the case of an impulse, the instant when the deflection has reached a maximum value and must be read. We shall refer to the first as the deflection period and the second as the ballistic period.

---

[3] Under any definite conditions the voltage sensitivity is equal to the current sensitivity divided by the resistance. It, therefore, is not necessary to introduce the idea of a voltage sensitivity as distinct from the current sensitivity. However, for those cases in which it is the voltage rather than the current which is the quantity to be measured or which is the independent variable, the operation of the galvanometer is much more readily understood if we refer to its voltage sensitivity rather than to its current sensitivity

In all cases the user of a galvanometer is concerned with the conditions which give critical damping; that is, the conditions which make the motion of the moving system just aperiodic (or just deadbeat). The damping often depends to a very marked degree upon the resistance of the circuit into which the galvanometer is connected. The resistance of the circuit (not including the resistance of the galvanometer) in which the motion of the moving system is critically damped will be referred to as the external critical resistance. In most cases it is an important operation constant of the galvanometer. If the apparatus with which the galvanometer is being used has a resistance between the terminals to which the galvanometer is connected different from the external critical resistance, critical damping can be brought about with most galvanometers of the moving coil type and with some of the moving magnet type. In some cases it is done by putting resistance in series with the apparatus and galvanometer, and in other cases resistance is put in parallel across the terminals to which the galvanometer is connected.

Sometimes it is desired that the galvanometer be approximately critically damped without special adjustment for all readings or settings of the apparatus with which it is used, when the resistance of the apparatus between the terminals to which the galvanometer is connected varies with the setting through wide limits. This condition is usually easily brought about by the use of two resistances, one connected in parallel and the other connected in series with the galvanometer. By a proper choice of the resistances, the damping can be made very nearly critical regardless of the resistance of the apparatus with which the galvanometer is used, but to do so necessarily reduces the sensitivity very materially. It is also possible to design a galvanometer so that, without a shunt or parallel resistance, it will be approximately critically damped when used in circuits of almost any resistance. This is accomplished by the use of suitable air dampers or by the use of an auxiliary winding closed upon itself. Sometimes the winding of a moving coil galvanometer is placed on a metal frame which serves also as the auxiliary closed circuit winding. The use of an auxiliary winding makes the construction of a galvanometer to have a high sensitivity to voltage or voltage impulse and a short deflection period much more difficult.

For general laboratory use it is desirable that the rate of change of the damping (or, more specifically, the rate of change of the deflection period) with the change in resistance of the external circuit shall be small. Its value, or something equivalent to it, might be considered as one of the operation constants. However, where a high or fairly high sensitivity is required it is better to make the adjustments necessary to give critical or approximately critical damping. Where this is done, the rate of change of the damping with change of the external resistance is of but little importance.

The operation constants with which the user of a galvanometer may be concerned, and the symbols here used to represent them, are as follows:

R = the external critical resistance,
T_d = the deflection period,
T_b = the ballistic period,
S_i = the current sensitivity,
S_e = the sensitivity to voltage in a circuit having a resistance giving critical damping,
S'_e = the sensitivity to voltage in a circuit of resistance exceeding the critical resistance,
S_q = the sensitivity to quantity or $\int idt$,
S_n = the sensitivity to $\int edt$ in a circuit having a resistance giving critical damping, and
S'_n = the sensitivity to $\int edt$ in a circuit having a resistance in excess of the critical resistance.

For any one of the four classes of measurements we need consider only the appropriate period and sensitivity, and usually the resistance of the apparatus between the terminals to which the galvanometer is connected, or the external critical resistance of the galvanometer.

2. THE INTRINSIC CONSTANTS

As has been pointed out above, the values of the operation constants necessarily depend upon the size, shape, and arrangement of the parts of the galvanometer; the kind of material used in the construction; the intensity of magnetization, etc. That is, they depend upon the values of the intrinsic or construction constants. The intrinsic constants and the symbols here used to represent them are as follows:

K = the inertia constant (the moment of inertia),
D = the damping constant (the ratio of the drag or retarding torque on the moving system to its rate of displacement, with the circuit open),

U = the restoring constant (the ratio of the restoring torque to the displacement),

G = the dynamic or displacing constant (the ratio of the displacing torque to the current), and

R_g = the resistance of the galvanometer.

Other symbols used and the quantities which they represent are as follows:

e = the voltage impressed in the circuit in which the galvanometer is connected,

i = the current in the circuit in which the galvanometer is connected,

θ = the angular displacement of the moving system,

t = the time,

s = the resistance of the shunt across the galvanometer terminals,

r = the resistance in series with the galvanometer,

R' = the resistance in series with the galvanometer if in excess of the external critical resistance,

r' = the resistance of an auxiliary closed winding,

g = the dynamic constant of an auxiliary closed winding,

D' = the damping constant with the auxiliary winding open, and

j, l, m, n, and p = constants defined by equations (66), (72), (49), (50), and (83).

3. OPERATION CONSTANTS IN TERMS OF INTRINSIC CONSTANTS

The equation generally accepted as representing the motion of the moving system of a galvanometer[4] is

$$K\frac{d^2\theta}{dt^2}+D\frac{d\theta}{dt}+U\theta=Gi \tag{1}$$

where i is the current in the winding or coil. This equation, however, is not in a convenient form, since as galvanometers are generally used the current, i, is affected by the motion of the moving system and so is not known. The current may, nevertheless, be expressed in terms of the impressed voltage, that is, the voltage having its seat in the apparatus with which the galvanometer is used, the voltage generated by the motion of the moving system and the constants of the circuit.

As is well known, especially to those who are familiar with the principles of operation of dynamo-electric machinery, that part of the electrical power supplied to the galvanometer which is converted into mechanical power is i times the generated or back voltage. Also the mechanical power is the torque, Gi, times the angular velocity, $\frac{d\theta}{dt}\cdot$ Since these two quantities must be equal it follows, therefore, that the generated voltage is $-G\frac{d\theta}{dt}\cdot$ Consequently, if $r+R_g$ is the resistance of the circuit and e is the impressed voltage,

---

[4] Gray, Absolute Measurements in Electricity and Magnetism, 2, Part II, p. 392.

$$i=\frac{e}{r+R_g}-\frac{G}{r+R_g}\frac{d\theta}{dt} \tag{2}$$

This value of i substituted in equation (1) gives as the equation of motion of the moving system

$$K\frac{d^2\theta}{dt^2}+\left(D+\frac{G^2}{r+R_g}\right)\frac{d\theta}{dt}+U\theta=\frac{Ge}{r+R_g} \tag{3}$$

If, for any reason, the galvanometer is shunted by a resistance, s, the current which would flow through the coil in case the impressed voltage only were effective, is $\frac{es}{rs+rR_g+sR_g}$ and in case the generated voltage only were effective, is $-\frac{G(s+r)}{rs+rR_g+sR_g}\frac{d\theta}{dt}\cdot$ Where R_g is the resistance of the galvanometer and r is the resistance of the apparatus with which it is used, or which is in series with the galvanometer, and in which there is the impressed voltage, e. Since the current through the coil is equal to that which would flow as a result of the impressed voltage only, plus that which would flow as a result of the generated voltage only, it follows that for this case the equation of motion is

$$K\frac{d^2\theta}{dt^2}+\left(D+\frac{G^2(s+r)}{rs+rR_g+sR_g}\right)\frac{d\theta}{dt}+U\theta=\frac{Gse}{rs+rR_g+sR_g} \tag{4}$$

These may be considered the general equations for the motion of the moving systems of galvanometers, excepting in those cases in which it is necessary to take into consideration either the effects of self or mutual inductance or of capacity. That the relations are at least approximately correct has been verified by numerous checks between values for constants found by using these relations and those values found by other means. It must not be presumed, however, that they are correct to a high order of accuracy, and it is not necessary for the purpose of this paper that they should be.

Equations of the type of (3) and (4) are considered in elementary textbooks on differential equations and in their solution there is obtained the auxiliary equation

$$a^2f+ag+h=0$$

in which f, g, and h are the coefficients of $\frac{d^2\theta}{dt^2}$, $\frac{d\theta}{dt}$ and θ. The form of the solution will depend upon whether

$$g^2 > 4fh, \ g^2 = 4fh \text{ or } g^2 < 4fh$$

as well as upon what function e is of t. When some change is made in the apparatus with which the galvanometer is used so that e suddenly assumes a new constant value, or when the moving system of the galvanometer is released from a deflected position, the moving system takes up the new position in the minimum time (and the motion is said to be just aperiodic or critically damped) if the two roots of the auxiliary equation just referred to are equal. That is, if

$$\frac{G^2}{r+R_g} + D = 2\sqrt{KU} \tag{5}$$

or if

$$\frac{G^2(s+r)}{rs+rR_g+sR_g} + D = 2\sqrt{KU} \tag{6}$$

The particular value of r which satisfies equation (5) is the external critical resistance of the galvanometer and is designated as R. Therefore it follows from equation (5) that

$$R = \frac{G^2}{2\sqrt{KU}-D} - R_g \tag{7}$$

If the resistance of the apparatus with which the galvanometer is used (measured between the terminals to which the galvanometer is connected) is less than the external critical resistance, then critical damping may be brought about by connecting the proper amount of resistance in series with the galvanometer. If the resistance of the apparatus with which the galvanometer is used is more than the external critical resistance of the galvanometer, critical damping may usually be brought about by connecting a resistance, s, of suitable value in parallel with the galvanometer. In this case the value of s must be chosen so that

$$sR'/(s+R') = R \tag{7a}$$

where R' represents the resistance of the apparatus.

If the galvanometer is critically damped without the use of a parallel resistance, it follows from equations (3), (5), and (7), that

$$K\frac{d^2\theta}{dt^2} + 2\sqrt{KU}\frac{d\theta}{dt} + U\theta = \frac{(2\sqrt{KU}-D)e}{G} \tag{8}$$

If a parallel resistance is used to bring about critical damping, it follows from equations (4), (6), (7), and (7a) that

$$K\frac{d^2\theta}{dt^2}+2\sqrt{KU}\frac{d\theta}{dt}+U\theta=\frac{(G^2-2R_g\sqrt{KU}+DR_g)e}{R'G} \tag{9}$$

and if conditions are such that the galvanometer has no appreciable effect upon the magnitude of the current, *i*, in the main circuit, then

$$K\frac{d^2\theta}{dt^2}+2\sqrt{KU}\frac{d\theta}{dt}+U\theta=\frac{(G^2-2R_g\sqrt{KU}+DR_g)i}{G} \tag{10}$$

Here, since the galvanometer is shunted, *i* is not the current in its winding or coil.

Equations (8), (9), and (10) are the general equations for the motion of the moving systems of critically damped galvanometers and are the equations on which the work which follows is based. Equation (8) applies in case critical damping is brought about without the use of a shunt, and the impressed voltage is the independent variable. Equation (10) applies in case the galvanometer is shunted to bring about critical damping, and the current may be considered the independent variable. Equation (9) applies in case it is necessary to use a shunt to bring about critical damping and when the impressed voltage, rather than the current, must be considered the independent variable. Equation (9) applies in the cases which are intermediate between those to which equation (8) applies and those to which equation (10) applies.

Following a change in the value of the voltage or current from one steady value to another, there results a change in the steady deflection. If the change in voltage is Δe, or current is Δi, and the resulting change in the steady deflection is $\Delta\theta$, the ratio of $\Delta\theta$ to Δe, or to Δi, is the sensitivity. Since, when the deflection becomes steady, both $\frac{d^2\theta}{dt^2}$ and $\frac{d\theta}{dt}$ are zero, inspection of equations (8), (9), and (10) shows that

$$S_e=\frac{2\sqrt{KU}-D}{GU} \tag{11}$$

$$S'_e=\frac{G^2-2R_g\sqrt{KU}+DR_g}{R'GU} \tag{12}$$

$$S_i=\frac{G^2-2R_g\sqrt{KU}+DR_g}{GU} \tag{13}$$

where S_i is the sensitivity of the galvanometer to current when connected in a circuit of high resistance, S_e is the sensitivity of the galvanometer to voltage having its seat in apparatus of resistance equal to the external critical resistance of the galvanometer, and S'_e is the sensitivity of the galvanometer to voltage in apparatus having a resistance R' in excess of the external critical resistance of the galvanometer, so that the galvanometer must be shunted to bring about critical damping.

If, instead of the voltage or current assuming a new constant value, it assumes a fairly large value for a very short time, after which it becomes zero or assumes its former value, an impulse is given to the moving system. If the time of the impulse is very short in comparison with the time of throw, during the impulse the second and third terms of the left-hand members of equations (8), (9), and (10) are very small in comparison with the first, so may be neglected. Then by a single integration over the time of the impulse it follows that

$$K\frac{d\theta}{dt}=\frac{2\sqrt{KU}-D}{G}\int e\,dt \tag{14}$$

$$K\frac{d\theta}{dt}=\frac{G^2-2R_g\sqrt{KU}+DR_g}{R'G}\int e\,dt \tag{15}$$

and

$$K\frac{d\theta}{dt}=\frac{G^2-2R_g\sqrt{KU}+DR_g}{G}\int i\,dt \tag{16}$$

While here no consideration is given to self-induced voltage, which may during a part of the impulse be of the same order of magnitude as e, it may easily be shown that no appreciable error is introduced on this account, unless the self-inductance is so large that the electrical time constant of the circuit is appreciable in comparison with the time of the throw of the moving system.

After the impulse the right-hand members of equations (8), (9), and (10) are zero, so that for each of the three cases the equation of the motion of the moving system is:

$$K\frac{d^2\theta}{dt^2}+2\sqrt{KU}\frac{d\theta}{dt}+U\theta=0 \tag{17}$$

The solution of this equation (which is a special form of equations (3) and (4) considered above) is as follows:

$$\theta=C_1\epsilon^{-\sqrt{U/K}t}+C_2t\epsilon^{-\sqrt{U/K}t} \tag{18}$$

where C_1 and C_2 are constants of integration and ϵ is the base of the Naperian logarithm. Here C_1 is zero, since at the end of the impulse both θ and t may be considered zero. Differentiation of equation (18) gives

$$\frac{d\theta}{dt} = -C_2 t\sqrt{U/K}\epsilon^{-\sqrt{U/K}t} + C_2\epsilon^{-\sqrt{U/K}t} \tag{19}$$

from which it follows that θ is a maximum when $t = \sqrt{K/U}$ or that

$$T_b = \sqrt{K/U} \tag{20}$$

where T_b is the time of throw[5] or the ballistic period. It also follows that C_2 is equal to the value of $\frac{d\theta}{dt}$ when $t = 0$, which is the value of $\frac{d\theta}{dt}$ as given by equation (14), (15), and (16). The substitution of these values for C_2 and t in equation (18) gives

$$S_n = \frac{\Theta}{\int e dt} = \frac{1}{\epsilon G}\left[2 - \frac{D}{KU}\right] \tag{21}$$

$$S'_n = \frac{\Theta}{\int e dt} = \frac{G^2 - 2R_g\sqrt{KU} + DR_g}{\epsilon R' G\sqrt{KU}} \tag{22}$$

$$S_q = \frac{\Theta}{\int i dt} = \frac{G^2 - 2R_g\sqrt{KU} + DR_g}{\epsilon G\sqrt{KU}} \tag{23}$$

where Θ is the maximum value of θ or the magnitude of the ballistic throw, and S_n, S'_n, and S_q are the sensitivities to voltage and current impulses.

From equation (18) it will be seen that the deflection reaches a maximum and then becomes zero after a long time. However, when $t = (2\pi + 1)\sqrt{K/U}$ the deflection has passed and is then only a little more than 1 per cent of its maximum value. Since, in returning from the deflected position, the motion follows the same law as when e is suddenly changed from one constant value to another, the system accomplishes nearly 0.99 part of its final steady deflection in a time equal to $2\pi\sqrt{K/U}$. For most purposes one is not concerned in reading deflections to as close as 1 per cent, so we shall consider that

$$T_d = 2\pi\sqrt{K/U} \tag{24}$$

where T_d is the deflection period. That is, we shall consider the deflection period to be the same as the complete undamped period.

---

[5] The effect of damping, especially critical damping, upon the time of throw or ballistic period and upon the ballistic sensitivity is discussed by Stewart, Physical Review, 16, p. 158, 1902. The effect of the damping by the current in a circuit of low resistance resulting from the voltage generated by the motion of the moving system is discussed by Jones, Proceedings of the Physical Society, 26, p. 75, 1914.

Collecting the equations representing the relations[6] between operation and intrinsic constants gives

$$R = \frac{G^2 - R_g(2\sqrt{KU} - D)}{2\sqrt{KU} - D} \tag{25}$$

$$T_d = 2\pi\sqrt{K/U} \tag{26}$$

$$T_b = \sqrt{K/U} \tag{27}$$

$$S_e = \frac{2\sqrt{KU} - D}{GU} \tag{28}$$

$$S'_e = \frac{G^2 - R_g(2\sqrt{KU} - D)}{R'GU} \tag{29}$$

$$S_i = \frac{G^2 - R_g(2\sqrt{KU} - D)}{GU} \tag{30}$$

$$S_n = \frac{1}{\epsilon G}\left[2 - \frac{D}{\sqrt{KU}}\right] \tag{31}$$

$$S'_n = \frac{G^2 - R_g(2\sqrt{KU} - D)}{\epsilon G\sqrt{KU}\,R'} \tag{32}$$

$$S_q = \frac{G^2 - R_g(2\sqrt{KU} - D)}{\epsilon G\sqrt{KU}} \tag{33}$$

It may be of interest to note that in case D is very small in comparison with $\sqrt{KU}$

$$S_e = \frac{2}{G}\sqrt{\frac{K}{U}} \tag{34}$$

and

$$S_n = \frac{2}{\epsilon G} \tag{35}$$

and in case $D = 2\sqrt{KU}$

$$S_i = \frac{G}{U} \tag{36}$$

$$S_q = \frac{G}{\epsilon\sqrt{KU}} \tag{37}$$

that is, the relations are much simpler than in the corresponding equations above.

---

[6] It should be understood that the magnitudes of the operation constants are to be expressed in the system of units in which the intrinsic constants are expressed and not in the units usually employed.

4. RELATIONS BETWEEN OPERATION CONSTANTS

The fact that a galvanometer has but five intrinsic constants is evidence that all of the relations given by equations (25) to (33) can not be independent and that there must be some relations between the operation constants. An inspection will show that there is a simple relation between the ballistic and deflection periods, and between the four sensitivities. Expressing the other operation constants in terms of R, T_d, and S gives

$$T_b = \frac{T_d}{2\pi} \tag{38}$$

$$S'_e = \frac{R}{R'} S_e \tag{39}$$

$$S_i = R S_e \tag{40}$$

$$S_n = \frac{2\pi S_e}{\epsilon T_d} \tag{41}$$

$$S'_n = \frac{2\pi R S_e}{R' T_d \epsilon} = \frac{R}{R'} S_n \tag{42}$$

$$S_q = \frac{2\pi R S_e}{\epsilon T_d} = R S_n \tag{43}$$

These equations show what should be expected from a galvanometer intended for use in class B work, if used with apparatus having resistance between galvanometer terminals in excess of the external critical resistance of the galvanometer, or when used in class A, C, or D work.

The way the sensitivity changes as the resistance of the apparatus (between galvanometer terminals) increases, keeping the damping critical either by resistance in series or in parallel, is shown in Fig. 1. The point where the direction of the curves changes abruptly is where it is necessary to change the resistance from series to parallel to keep the damping critical, or where the resistance of the apparatus is equal to the external critical resistance of the galvanometer.

III. GENERAL DESIGN

1. NUMBER OF OPERATION AND INTRINSIC CONSTANTS

Equations (25) to (33) give the relations between the operation and intrinsic constants; that is, they enable one to calculate the values of the operation constants for known values of the intrinsic constants. But in the general design of galvanometers the problem is to find values or sets of values for the intrinsic constants such as will give specified values for the operation[7] constants. An inspection of the equations shows that as they stand it would be difficult to use them for this purpose. For example, consider the design of a galvanometer for use with a bridge having a specified resistance between the terminals to which the galvanometer is to be connected, to give a specified deflection per unit of voltage which would be between the galvanometer terminals of the bridge with the galvanometer circuit open, and to come to rest in a deflected or zero position in specified time. The problem, then, is to find a set of values for the intrinsic constants such as will give the specified values for R, T_d, and S_e.

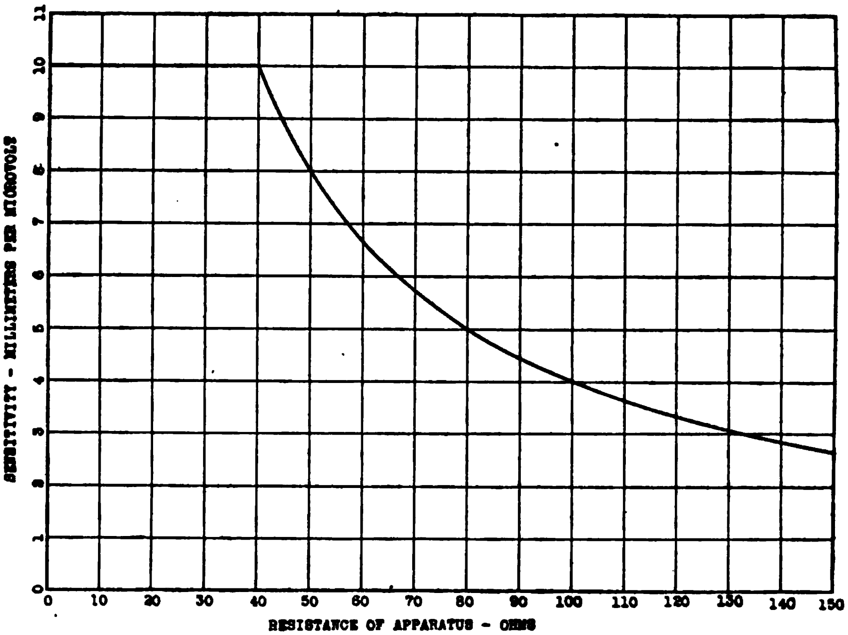


FIG. 1.—*Curve showing how the sensitivity to voltage changes as the resistance of the apparatus, with which the galvanometer is used, is changed. The curve applies for a galvanometer having an external critical resistance of 40 ohms and a sensitivity of 10 millimeters per microvolt*

---

[7] The values of the five intrinsic constants of a galvanometer may be determined from measurements of five independent operation constants, or if one or more of the intrinsic constants is measured directly, then the remaining intrinsic constants may be determined from measurements of four or fewer independent operation constants. The equations representing the relations between the intrinsic constants and the measured operation constants may be used for calculating the values of the intrinsic constants necessary to give previously selected values for operation constants. For example, we have the equations given in this Bulletin, 6, p. 361, 1910. These could be used for determining values for the inertia constant, the damping constant, the restoring constant, and the dynamic constant necessary to give previously selected values for the alternating-current sensitivity, the alternating-voltage sensitivity, the direct-current sensitivity, and the resonating frequency; the value for the resistance of the galvanometer being chosen arbitrarily.

The relations between the operation constants and the intrinsic constants are given by equations (25), (26), and (28). However, it will be seen that one can not readily choose a set of values such that when they are substituted in these equations they give the value specified for each of the three operation constants. Even if he should find a set of values which would give the specified values for the operation constants, they would probably be such as would make the detail design and construction unnecessarily difficult. It is therefore desirable that the matter be investigated for the purpose of establishing, if possible, a definite procedure for finding values for the construction constants of galvanometers such as will give specified values for the operation constants, pertaining to each of the four different classes of work considered above. It is also important that the procedure enable us to know definitely the limits to the values for each of the intrinsic constants and something of the relations between them.

It has been shown above that there are only three independent relations expressed by equations (25) to (33). It has also been pointed out that for any class of measurements the user of a galvanometer is concerned, at most, with only three operation constants, while the galvanometer has five intrinsic constants. This suggests that possibly values for two or more of the intrinsic constants may be chosen arbitrarily [8] or within limits and values then calculated for the others such as will give specified values for the operation constants.

2. INTRINSIC CONSTANTS IN TERMS OF OPERATION CONSTANTS

An inspection of equations (25) to (33) shows that all can be satisfied with a zero value for both the resistance, R_g, and the damping constant, D. But the construction of a galvanometer for which either R_g or D is zero is impossible, though in some cases either or both may be made so small as to have no appreciable effect. If, however, the galvanometer is to have a high sensitivity to voltage or voltage impulse in a circuit of low resistance, then neither can conveniently be made so small that its effect may be neglected.

Considering the external critical resistance R, the deflection period T_d, the sensitivity S_e, the resistance R_g, and the damping constant D as fixed, a solution of equations (25), (26), and (28) for the inertia constant K, the restoring constant U, and the dynamic constant G, shows that the values for these constants are complex (contain a real and imaginary part) unless

---

[8] A consideration of the matter from the standpoint of the power available for producing a deflection, the deflection period, and the energy necessary to produce a deflection shows that, in many cases, a value for none of the intrinsic constants other than the resistance can be chosen arbitrarily, except within limits.

$$D \leqq \frac{T_d^2}{4\pi^2 S_e^2 (R+R_g)} \tag{44}$$

In any design possible of construction, therefore, D must have a value less than this maximum which depends upon the values desired for the operation constants and the value chosen for the resistance R_g, which, however, has no definite upper limit. The values for R_g may, therefore, be chosen entirely arbitrarily, while the values for D must be chosen less than a certain maximum. Values for others of the intrinsic constants, instead of these two, may, within limits, be chosen arbitrarily, but the relations[9] obtainable from equations (25), (26), and (28) which give most promise of being of use in the design of galvanometers for use in class B measurements are

$$D \leqq \frac{T_d^2 m}{4\pi^2 S_e^2 R} \tag{45}$$

$$K = \frac{T_d^3 mn}{4\pi^3 S_e^2 R} \tag{46}$$

$$U = \frac{T_d mn}{\pi S_e^2 R} \tag{47}$$

$$G = \frac{T_d n}{\pi S_e} \tag{48}$$

where

$$m = R/(R+R_g) \tag{49}$$

and

$$n = \tfrac{1}{2}\left[1 \pm \sqrt{1 - 4\pi^2 D S_e^2 R / T_d^2 m}\right] \tag{50}$$

The ± sign in equation (50) shows that even after values are chosen for R_g and D there still remains a choice between two sets of values for K, U, and G. It will be seen, too, that if D is small in comparison with its maximum possible values, each value in one set is much smaller than the corresponding value in the other set.

---

[9] Equations somewhat similar to (45) to (48) were published by Jaeger (Annalen der Physik, **20**, p. 76, 1906) and discussed briefly with reference to changes in a particular galvanometer necessary for a certain change in the period and total critical resistance. Later Diesselhorst (Zeitschrift für Instrumentenkunde, **31**, p. 250, 1911) used the same equations for finding values for the inertia constant, the damping constant, the restoring constant, and the dynamic constant necessary to give chosen values for the sensitivity, the period, the total critical resistance, and a factor depending upon the logarithmic damping on open circuit. Neither of these authors separates the resistance of the galvanometer from its total critical resistance. That is, they do not make a complete distinction between those of the operation constants with which the user of the galvanometer is concerned and the intrinsic constants, and, as the equations are stated, it would seem that an unnecessary condition is imposed on account of the way the factor depending upon the logarithmic decrement on open circuit enters. In reality no unnecessary condition is imposed, since the user of a galvanometer does not care what the decrement on open circuit is and, consequently, the designer may choose any value for the factor which seems easily realized in the construction.

If the smaller values are chosen, the construction may be much more difficult and the completed instrument may be much more delicate than is necessary, considering the values for its operation constants and the values chosen for its resistance and damping constant. Galvanometers in which more than half of the critical damping is caused by the current which flows in the main winding, as a result of the voltage generated by the moving system, have the larger values for K, U, and G; others have the smaller values. From the standpoint of the design there is a decided difference, depending on whether the + or the − sign, which occurs here and later, is used, and sometimes it will be desirable to use one and sometimes the other.

In the design of galvanometers for use in class A measurements the relations obtainable from equations (25), (26), and (30), which give most promise of being of value, are

$$D \leqq \frac{T_d{}^2 Rm}{4\pi^2 S_1{}^2} \tag{51}$$

$$K = \frac{T_d{}^3 Rmp}{4\pi^3 S_1{}^2} \tag{52}$$

$$U = \frac{T_d Rmp}{\pi S_1{}^2} \tag{53}$$

$$G = \frac{T_d Rp}{\pi S_1} \tag{54}$$

where

$$m = R/(R+R_g) \tag{55}$$

and

$$p = \tfrac{1}{2}\left[1 \pm \sqrt{1 - 4\pi^2 S_1{}^2 D/T_d{}^2 Rm}\right] \tag{56}$$

Here, in case $T^2 Rm$ is very large in comparison with $4\pi^2 S_1{}^2 D$ and the negative sign of equation (56) is used, expansion of the radical shows that p may be considered equal to $\pi^2 S_1{}^2 D/T_d{}^2 Rm$. This value of p substituted in equations (52), (53), and (54) gives

$$K \doteq \frac{DT_d}{4\pi} \tag{57}$$

$$U = \frac{\pi D}{T_d} \tag{58}$$

$$G = \frac{\pi D S_1}{T_d} \tag{59}$$

These equations[10] may also be obtained directly from the relations

$$D = 2\sqrt{KU},\ T_d = 2\pi\sqrt{K/U} \text{ and } S_1 = G/U \tag{60}$$

---

[10] In equations (59) and (75) we have considered that $m=1$, which we may do, since R is large in comparison with R_g or there is a condenser in series in the circuit.

which apply in case the instrument is critically damped with the main galvanometer circuit open.

In the same way, it follows from equations (25), (27), and (31) that the relations most likely to be of service in the design of galvanometers for use in class D measurements are

$$D \leqq \frac{m}{\epsilon^2 S_n^2 R} \tag{61}$$

$$K = \frac{2T_b m j}{\epsilon^2 S_n^2 R} \tag{62}$$

$$U = \frac{2mj}{\epsilon^2 T_b S_n^2 R} \tag{63}$$

$$G = \frac{2j}{\epsilon S_n} \tag{64}$$

where

$$m = R/(R+R_g) \tag{65}$$

and

$$j = \tfrac{1}{2}\left[1 \pm \sqrt{1-\epsilon^2 D S_n^2 R/m}\right] \tag{66}$$

Finally from equations (25), (27), and (33) it follows that the relations which give most promise of being of service in the design of galvanometers for use in class C measurements are

$$D \leqq \frac{Rm}{\epsilon^2 S_q^2} \tag{67}$$

$$K = \frac{2T_b R m l}{\epsilon^2 S_q^2} \tag{68}$$

$$U = \frac{2Rml}{\epsilon^2 S_q^2 T_b} \tag{69}$$

$$G = \frac{2Rl}{\epsilon S_q} \tag{70}$$

where

$$m = R/(R+R_g) \tag{71}$$

and

$$l = \tfrac{1}{2}\left[1 \pm \sqrt{1-\epsilon^2 D S_q^2/Rm}\right] \tag{72}$$

In case Rm is large in comparison with $\epsilon^2 S_q^2 D$ and we use the negative sign of equation (72), expansion of the radical shows that we may consider $l = \epsilon^2 S_q^2 D/4Rm$. This value of l substituted in equations (68), (69), and (70) gives

$$K = \frac{T_b D}{2} \tag{73}$$

$$U = \frac{D}{2T_b} \tag{74}$$

$$G = \frac{\epsilon S_q D}{2} \tag{75}$$

Equations (57), (58), (59), (73), (74), and (75) apply only in those cases in which critical damping is brought about under conditions in which the voltage generated by the motion of the moving system has no appreciable effect upon the magnitude of the current in the main winding. If the damping is supplied mainly by a current induced in an auxiliary winding closed upon itself, and if g and r' are its dynamic constant and resistance, and D' is the damping constant with both main and auxiliary winding open, the constants of the auxiliary winding must be such that

$$\frac{g^2}{r'}=2\sqrt{KU}-D' \tag{76}$$

If the galvanometer is to be used in a circuit whose resistance, $R'+R_g$ including that of the galvanometer, is not excessively high, then for critical damping it is necessary that

$$\frac{g^2}{r'}=2\sqrt{KU}-D'-\frac{G^2}{R'+R_g} \tag{77}$$

It should be noted that the operation constants all appear on the left-hand side of the equations, and also that those of equations numbered (45) to (50) pertain to class B measurements, those of equations numbered (51) to (59) pertain to class A measurements, those of equations numbered (61) to (66) pertain to class D measurements, and those of equations numbered (67) to (75) pertain to class C measurements.

These equations show the maximum value the damping constant of a galvanometer can have and have chosen values for its resistance, external critical resistance, period, and sensitivity. They also show what values the inertia constant, the restoring constant, and the dynamic constant must have in order that a galvanometer may have chosen values for its resistance, damping constant, external critical resistance (and in some cases the resistance of the apparatus with which the galvanometer is to be used), and the particular period and sensitivity with which we may be concerned. The equations may, therefore, be used in the general design of galvanometers.

3. PROCEDURE IN THE GENERAL DESIGN

Since a value for the resistance of the galvanometer may be chosen arbitrarily and any value taken for its damping constant, less than a certain maximum shown by the first of each set of equations, much is left to the judgment of the person making the general design, and the difficulties encountered in the detail design and construction and the performance of the galvanometer, in matters other than the values of its operation constants, will depend in no small degree upon the judgment used.

In carrying out a general design the first thing to do is to choose a value for the resistance of the galvanometer, and if one is entirely at a loss in the matter, he may take it equal to that of the rest of the circuit in which the galvanometer is to be used, that is, take R_g equal to R. This makes m, which occurs in most of the equations, equal to one-half. Using this value for m in the first of the set of equations pertaining to the class of work in which it is intended that the galvanometer shall be used, gives the maximum value D can have. Taking D equal to half this maximum value and using the + sign in the last equation of the set makes n (or l or p or j) equal to 0.85. Using these values for m and n the corresponding values for K, U, and G can readily be calculated. This gives us a set of values for the intrinsic constants such as will give the specified values for the operation constants.

While it is not to be presumed that this particular set of values will lend itself most readily to the detail design and construction, it may be used in making a preliminary detail design. A little consideration of the detail design will show, in most cases, that *the resistance of the galvanometer can, to advantage, be made much less than the external critical resistance,* and in a moving coil type of galvanometer, of low external critical resistance, the larger part of the resistance may be in the suspensions rather than in the coil. Ordinarily, such a preliminary detail design will enable us to choose revised values for R_g and for D, such that with the corresponding values for K, U, and G they constitute a set of values for the intrinsic constants which are more easily realized in the detail design and construction.

To get the best results in the general design of a galvanometer, one should be reasonably familiar with the performance and construction of somewhat similar galvanometers (know both their operation and their intrinsic constants) and know fairly definitely the properties of the materials available for the construction of the proposed galvanometer. Usually the general design should be considered as subject to slight modifications until the size of the mirror, the size of the wire, number of turns of and dimensions of the winding, the strength of the magnetic field, the kind of material, section and length of the suspensions, and most of the details of construction are decided upon.

4. DESIGN FOR CURRENT SENSITIVITY

Here the problem is to design a galvanometer which shall be suitable for use in class A measurements, that is, in those measurements in which the galvanometer serves to detect or measure a small current in a circuit of high resistance. (See p. 212.) In general, this resistance may be presumed to be so high that no account need be taken of the effect of the resistance of the galvanometer, or of the voltage generated by the motion of its moving system upon the magnitude of the current. Stating the situation in a slightly different way, the power which can reasonably be dissipated in the resistance of the galvanometer ($R_g i^2$) plus that which can be converted into mechanical power ($i\ e'$, where e' is is the voltage generated by the motion of the moving system) is so small in comparison with the power supplied to the circuit that no account need be taken of it. We may, therefore, make the resistance, or any other of the intrinsic constants, practically as large as we please.

More specifically, the problem is to design a galvanometer to be critically damped in a circuit of very high resistance and have a certain deflection period and current sensitivity.

Equations (51) to (56), inclusive, give the relations which must be satisfied in the general design. Here, R is the resistance which, when connected in series with the galvanometer, gives critical damping. With the galvanometer connected in a circuit of very high resistance, it is the value of the shunt necessary to produce critical damping. If there is a second winding for which the ratio of dynamic constant to resistance is such as will, in itself, give critical damping, then the shunt may be dispensed with, that is, R may be taken as indefinite. There is, therefore, no definite limit for the value of R. It is desirable, however, either to have a shunt of only moderately high resistance or to dispense with it entirely. If R is to be only moderately high, the first matter to be decided upon in the general design is the resistance of the galvanometer. In this choice much will depend upon the size and properties (especially magnetic impurities and thickness of the insulation) of the wire available for winding the coil; the size and kind of wire available for the suspensions; the period, sensitivity, size of mirror, and ruggedness of the instrument desired; and the skill of the person who is to construct it. If the sensitivity is to be high the winding should be of fine wire, the number of turns should be fairly large, and the magnetic field should be strong. However, there is little or no advantage in increasing the number of turns to the point at which the inertia constant increases as rapidly as the dynamic constant.

Having decided upon a value for the resistance of the galvanometer, experience shows that the external critical resistance may be chosen from 2 to 20 times R_g, the resistance of the galvanometer (10 to 100 times R_g if the deflection period is long). Next, a value may be chosen for the damping constant D. This value must necessarily be less than the maximum corresponding to the chosen values for the resistances and specified values for the deflection period and current sensitivity as shown by equation (51). The corresponding values for the inertia constant K, the restoring constant U, and the dynamic constant G may then readily be calculated from equations (52) to (56), inclusive, using the positive sign in equation (56). The preliminary values for the intrinsic constants, found in this way, may be modified to suit better the conditions met in the detail design.

As an example, assume that a galvanometer is desired to have a deflection period of six seconds, a current sensitivity of 2000 mm per microampere and be critically damped with a resistance in parallel of 2000 ohms; that is, a galvanometer for which

$$T_d = 6,\ S_i = 2000, \text{ and } R = 2000$$

Here the sensitivity and resistance are expressed in the units commonly used, while up to this point it has been assumed that all quantities would be expressed in cgs units or in the same system of units.

Expressing the current sensitivity in terms of the deflection on a scale 1 meter in front of the mirror in millimeters per microampere, the resistances in ohms, the deflection period in seconds, and the intrinsic constants, other than the resistance of the galvanometer, in cgs units, requires a change in the constant in the equations expressing the relations between the various constants. Making this change in equations (51) to (56), which give the relations which must be satisfied in this case, they may be written as follows:

$$D \leqq \frac{T_d^2 Rm}{S_i^2} \tag{78}$$

$$K = \frac{0.32 T_d^3 Rmp}{S_i^2} \tag{79}$$

$$U = \frac{12.7 T_d Rmp}{S_i^2} \tag{80}$$

$$G = \frac{64\,000 T_d Rp}{S_i} \tag{81}$$

where

$$m = R/(R + R_g) \tag{82}$$

and

$$p = \tfrac{1}{2}\left[1 \pm \sqrt{1 - S_1 D/TRm}\right] \tag{83}$$

From experience with other galvanometers, we would judge that it would be convenient to make the coil and suspensions in such a way as to have a resistance in the neighborhood of 200 ohms. Using this value for R_g and 2000 for R, it follows from equation (82) that

$$m = 0.91$$

and using this value for m and the specified values for the operation constants, it follows from equation (78) that

$$D \leqq 0.016$$

Taking

$$D = 0.008$$

gives, from equation (83),

$$p = 0.85$$

Values for K, U, and G are then obtained from equations (79), (80), and (81), using these values for m and p and the specified values for the operation constants. Proceeding in this way gives

$$K = 0.027,\ D = 0.008,\ U = 0.029$$

$$G = 330\,000, \text{ and } R_g = 200$$

These constitute a set of values for the intrinsic constants which give the specified values for the operation constants.

These values for the period, current sensitivity, and external critical resistance are those given by the Leeds & Northrup Co.[11] for their type of high sensitivity galvanometer. The value chosen for the resistance, however, is considerably less than the value which they give. Consequently, their values for the other intrinsic constants must differ slightly from these values.

It is to be understood that these values for the intrinsic constants would, in all probability, be changed slightly to better satisfy conditions met in the detail design. However, a change of a hundred ohms in the resistance of the galvanometer, so that we could use a particular size of wire that might be available, would not necessitate any very appreciable changes in the other intrinsic constants. If, on considering the detail design, it should be found that it would be better to have all the intrinsic constants larger, all that would be necessary would be to choose a correspondingly larger value for R.

---

[11] See Leeds and Northrup, Bulletin No. 228.

In designing a galvanometer to be critically damped without a shunt, the simpler equations (57), (58), and (59) may be used. Changing the constant of the latter to correspond with the unit of sensitivity used here, these may be rewritten as follows

$$K = 0.080 T_d D \tag{84}$$

$$U = 3.14 D/T_d \tag{85}$$

$$G = 15700 S_1 D/T_d \tag{86}$$

It will be noticed that the resistance of the galvanometer does not appear here and that there are only three conditions to be satisfied. Therefore, in addition to the resistance any other one of the intrinsic constants may be chosen entirely arbitrarily. The problem of the design, however, is not materially different from that just considered, except that some means must be provided for producing the necessary damping, since conditions are such that the voltage generated by the motion of the moving system can have no appreciable effect upon the magnitude of the current in the winding. If this is to be accomplished by an auxiliary winding closed upon itself, the constants of this winding may be readily calculated after K and U are determined, providing D', the damping constant with both main and auxiliary windings open, is small in comparison with $\sqrt{KU}$ or is known approximately. From equation (76) it follows that the relation which must be satisfied is

$$\frac{g^2}{r'} = \left[2\sqrt{UK} - D'\right] \times 10^9 \tag{87}$$

where g is the dynamic constant of the auxiliary winding in cgs units and r' its resistance in ohms.

In case one does not care to work out the details of a design to such an extent as will give specified values for the operation constants and yet wishes to construct a galvanometer having a high current sensitivity and a short deflection period, he should make the ratio of the value for the dynamic constant to the value for the inretia constant[13] as large as practicable. This follows from equations (84) and (86), which shows that for this case

$$\frac{S_1}{T_d^2} = \frac{51G}{K} \times 10^{-7} \tag{88}$$

---

[13] Mather, Philosophical Magazine, 29, p. 434; 1890.

5. DESIGN FOR VOLTAGE SENSITIVITY

Here the problem is to design a galvanometer which shall be suitable for use in class B measurements, that is, in those measurements in which the galvanometer serves to detect or measure a small voltage in a circuit of fairly low resistance. (See p. 213.) The resistance of the galvanometer and, during the time the deflection is changing, the voltage generated by the motion of its moving system have a marked effect upon the magnitude of the current, and consequently upon the magnitude of the torque acting upon the moving system.

Usually the apparatus with which the galvanometer is used (and in which, under definite conditions, there is a voltage to be detected or measured) has a certain resistance between the terminals to which the galvanometer is connected. If this resistance is R and the voltage e, the maximum current that may be drawn from these terminals is e/R and the power which may be dissipated in apparatus connected between the terminals can not under any condition be more than $e^2/4R$. This, therefore, is the maximum possible value for power available for producing a deflection of the galvanometer.

However, except by a motion of the moving system, this electrical power can not be converted into mechanical power. Therefore, the amount of energy available for producing a deflection of the galvanometer is $T_d e^2/4R$. The potential energy represented by the deflection must necessarily be considerably less than this amount, since the displacement of the moving system takes place according to a particular law, as shown by equation (18), so that the back or generated voltage is not, except at certain instances, of the magnitude necessary for galvanometer to receive the maximum available power. Further, some power is lost in the resistance of the winding and in air friction, and in the auxiliary closed winding, if there is one.

The problem, therefore, is very different from that which has just been considered. Instead of having all the power one might care to dissipate in the resistance of the galvanometer and use in producing a deflection, the amount of power available is definitely limited. Consequently all possible ways in which the power is used, such as in the resistance of the winding, in the damping frame or auxiliary winding, in case there is to be one, as well as in air friction and in twisting the suspensions or turning the magnet, it must considered. It might, therefore be better to speak of the power sensitivity, or possibly the energy sensitivity, rather than the voltage sensitivity. More specifically, the problem is the design of a galvanometer to be critically damped when connected to an external circuit having a resistance R, to have a certain sensitivity S_e to voltage in this circuit, and to have a certain deflection period T_d.

Equations (45) to (50) give the relations which must be satisfied. If the sensitivity is expressed as the deflection on a scale 1 meter in front of the mirror caused by an impressed voltage of 1 microvolt, the resistances are expressed in ohms and the other quantities are expressed in cgs units, these equations may be written as follows:

$$D \leqq \frac{T_d^2 m}{S_e^2 R} \tag{89}$$

$$K = \frac{0.32 T_d^3 mn}{S_e^2 R} \tag{90}$$

$$U = \frac{12.7 T_d mn}{S_e^2 R} \tag{91}$$

$$G = \frac{64\,000 T_d n}{S_e} \tag{92}$$

where

$$m = R/(R_g + R) \tag{93}$$

and

$$n = \tfrac{1}{2}\left[1 \pm \sqrt{1 - DRS_e^2/T_d^2 m}\right] \tag{94}$$

The first thing to be done is to decide upon a value for R_g, the resistance of the galvanometer. This value when substituted in equation (93) gives a value of m. Then from equation (89) the maximum possible value for D, the damping constant, is obtained. Choosing a smaller value for D, a value for n is obtained from equation (94). These values for m and n, and the specified values for the operation constants substituted in equations (90), (91), and (92) give values for the remaining intrinsic constants K, U, and G.

It will be observed that the higher the sensitivity and the shorter the deflection period desired, and the higher the resistance of the apparatus with which the galvanometer is to be used, and also the higher the resistance of the galvanometer is made, the smaller[13] D, K, U, and G must be. For galvanometers of high sensitivity and short period the difficulties met in the detail design and construction become greater the smaller we attempt to make the inertia and restoring constants. In the general design of such galvanometers we should therefore aim to keep these constants about as high as is possible. Since particular values usually are desired for T_d, R, and S_e the only place where there can be much choice is in the values of m and n, which should be kept as near unity as is practicable. That is, the values for R_g and D should be so chosen that R_g is small in comparison with R, D is small in comparison with its maximum possible value, and the plus sign in equation (94) should be used. The procedure given here is one that we have been using for the past three years, and a fairly large number of general designs have been made. In a few cases the corresponding detail designs have been worked out and the galvanometers constructed.

---

[13] The value of G, however, is but little affected by the value of R, of R_g, or of T_d.

For example, let us consider the general design of a moving coil galvanometer to be critically damped with an external resistance of 20 ohms, to have a deflection period of 10 seconds, and a sensitivity of 20 mm per microvolt, that is, have

$$R=20,\ T_d=10,\ \text{and}\ S_e=20$$

From experience in the construction of sensitive galvanometers we know that for the suspensions of this galvanometer very fine wire must be used, and that it would be difficult to make their resistance much less than 10 ohms. We also know that there need be no difficulty in making the coil so as to have a resistance of less than 5 ohms. Taking $R_g=12$ gives, from equation (93), $m=0.62$, and this value of m gives, from equation (94), $D\leqq 0.008$. From experience in the construction of somewhat similar galvanometers we know, if we are to use an approximately uniform radial field with a coil 8 to 10 mm wide and 10 to 15 mm long, we would have difficulty in making the damping constant much less than 0.004. Taking this value for D gives, from equation (94), $n=0.85$. Values for the remaining intrinsic constants are then obtained from equations (90), (91), and (92) by substituting these values for m and n and the specified values for the operation constants. This procedure gives as a complete set of values

$$K=0.021,\ D=0.004,\ U=0.0084$$
$$G=19\ 500,\ \text{and}\ R=12$$

The galvanometers[14] which we designate as type M have (with certain adjustments) very nearly these values for their intrinsic constants.

---

[14] Wenner, Weibel, and Weaver, Physical Review, 8, p. 497; 1914.

It may be of interest to notice that the maximum values possible for the different intrinsic constants are as follows:

$$K = 0.040,\ D = 0.008,\ U = 0.016$$

$$G = 23\,000, \text{ and } R_g \text{ no limit}$$

and that K, U, and G can be made to have these values only in case R_g can be made very small in comparison with R, and D can be made very small in comparison with its maximum possible value. It may also be of interest to notice that should a galvanometer be desired having the same external critical resistance and sensitivity but a deflection period only half as long, the inertia constant would necessarily be only one-eighth as large.[15] Also the suspension or restoring constant, instead of being larger, would necessarily be only about one-half as large.

6. DESIGN FOR $\int idt$ SENSITIVITY

Here the problem is to design a galvanometer suitable for use in class C measurements, that is, in those measurements in which the galvanometer serves to measure a small quantity or current impulse. (See p. 213.) Usually the current impulse results from condenser charge or discharge, so that while resistance in the circuit affects the duration, in most cases, it does not affect the magnitude of the impulse.

Only where the resistance is excessively high, much higher than there is any need for making the winding of a galvanometer, is there any appreciable reduction in the throw because of the resistance. The problem of the general design is therefore somewhat similar to that in which the sensitivity to be considered is to current, except that the relation between the ballistic period and the intrinsic constants is very different from the relation between the deflection period and the intrinsic constants. More specifically, the problem is to design a galvanometer to have certain particular values for its ballistic period and $\int idt$ or quantity sensitivity, and be critically damped on open circuit or when shunted with a fairly high resistance.

For example, consider the design of a galvanometer to be critically damped on open circuit, to have a ballistic period of two seconds and an $\int idt$ sensitivity of 1000 mm per microcoulomb. The problem, then, is to design a galvanometer for which

$$T_b = 2,\ R = \infty, \text{ and } S_q = 1000.$$

---

[15] For a quick-acting sensitive galvanometer the advantage of making the inertia constant much smaller than has previously been customary is pointed out by Moll, Proceedings of the Koninkijke Akademie van Wetenschappen te Amsterdam, **16**, p. 149; 1913.

Let us assume that we will make the resistance any value which the detailed design shows will be convenient, and that we will make $K = 0.10$ cgs units. Since the $\int idt$ sensitivity is expressed as the deflection on a scale 1 meter in front of the mirror in millimeters per microcoulomb, if the other quantities are to be expressed in cgs units, then equations (73), (74), and (75), which apply in this case, may be written as follows:

$$D = 2K/T_b \tag{95}$$

$$U = K/T_b^2 \tag{96}$$

$$G = 13600\, S_q K T_b \tag{97}$$

From these the values of D, U, and G may be readily obtained by a substitution of the particular values of K, T_b, and S_q. This gives for the intrinsic constants

$$D = 0.10,\ K = 0.10,\ U = 0.025$$

$$G = 860000, \text{ and } R_g = \text{any value}$$

If the galvanometer is to be of the moving coil type and have the pole pieces and core so shaped as to give practically a radial field, we know from experience that the damping constant D' (resulting mainly from air friction) is likely to be in the neighborhood of 0.03 unless some effort is made to make it unusually small. For critical damping the difference between D and D', amounting to 0.07, must be provided for in some way. If this is to be by an auxiliary winding closed upon itself, then from equation (76) the relation between its dynamic constant g expressed in cgs units and its resistance r' expressed in ohms must be such that

$$\frac{g^2}{r'} \times 10^{-9} = 0.07$$

If conditions are met in the detail design which show that there would be an advantage in having larger or smaller values for the intrinsic constants, there would be no difficulty in finding a new set differing widely from these yet giving the same values for the operation constants.

For a galvanometer to be shunted so that critical damping is brought about by current induced in the main winding instead of an auxiliary winding, the problem of the general design is not materially different. A value must be chosen both for the resistance of the galvanometer and for the resistance of the shunt. These, together with the values for the operation constants, give from equations (71) and (67) an upper limit for the damping constant. Choosing a smaller value for the damping constant, values for the remaining intrinsic constants may be calculated from equations (68), (69), and (70). Here the constants of the equations must be changed unless all qauntities are expressed in cgs units.

7. DESIGN FOR $\int e\,dt$ SENSITIVITY

Here the problem is to design a galvanometer which shall be suitable for use in class D measurements, that is, in those measurements in which the galvanometer serves to detect or measure small voltage impulses in circuits of fairly low resistance. (See p. 213.)

Both the resistance of the galvanometer and the voltage generated by the motion of the moving system have a marked effect upon the magnitude of the current (the latter, of course, only while the deflection is changing) and consequently upon the magnitude of the ballistic throw. The problem of the design is therefore somewhat similar to that in which the sensitivity to be considered is to voltage. The effects of the resistance of the winding, of the damping on open circuit, and of the voltage generated by the motion of the moving system are very similar. More specifically, the problem is to design a galvanometer which shall be critically damped when connected to an apparatus having a certain resistance, have a certain sensitivity to a voltage impulse in the apparatus, and have a certain ballistic period.

The relations which must be satisfied are given by equations (61) to (66), inclusive. In case the sensitivity is expressed as the deflection, on a scale 1 meter in front of the mirror, in millimeters per microvolt-second, the resistances are expressed in ohms and the other quantities are expressed in cgs units, these relations may be written as follows:

$$D \leq \frac{5.4m}{S_n^2 R} \tag{98}$$

$$K = \frac{10.8 T_b m j}{S_n^2 R} \tag{99}$$

$$U = \frac{10.8 m j}{T_b S_n^2 R} \tag{100}$$

$$G = \frac{147\,000 j}{S_n} \tag{101}$$

$$m = R/(R + R_g) \tag{102}$$

$$j = \tfrac{1}{2}\left[1 \pm \sqrt{1 - DRS_n^2/5.4m}\right] \tag{103}$$

In carrying out any particular design the first thing to be decided upon is the resistance of the galvanometer, and it will be observed that, in general, the higher the value chosen for the resistance the smaller all the other intrinsic constants must be made. For sensitive galvanometers, difficulties are met in the detailed design and construction if the inertia and restoring constants must be small. It is therefore desirable to choose a value for R_g which, if practicable, is small in comparison with R. Having decided upon a value for R_g, a value must be chosen for the damping constant, D. If practicable, this value should be not more than half the maximum possible value as given by equation (98). A much larger value for D would require making K and U considerably smaller.

For example, let us consider the general design of a galvanometer to be critically damped in a circuit of 25 ohms, not including the resistance of the galvanometer; to have a ballistic period of 1 second, and a sensitivity of 1 mm per microvolt-second. That is a galvanometer for which

$$R = 25,\ T_b = 1,\text{ and } S_n = 1.$$

If the galvanometer is to be of the moving coil type, from experience in the construction of similar galvanometers we know that it would be difficult to make the resistance much less than 10 ohms. Taking R_g as 10 gives, from equation (102), $m = 0.71$. This value m gives, from equation (98), 0.038 as the maximum possible value for D. Taking $D = 0.019$ gives, from equation (103), $j = 0.85$. Values for the remaining intrinsic constants are then readily obtained from equations (99), (100), and (101), and we have as the complete set

$$K = 0.062,\ D = 0.019,\ U = 0.062$$

$$G = 62\,600,\text{ and } R_g = 10.$$

With suitable material there should be little or no difficulty in carrying out the detailed design and construction so as to obtain very nearly these intrinsic constants. A consideration of the detailed design would, no doubt, suggest some slight changes in the general design.

8. DETAIL DESIGN

The detail design consists in deciding upon the number of turns and shape of the winding, the size and kind of wire to be used, the strength of the magnetic field, or the size, shape, etc., of the magnet; the length, size, shape, and kind of material to be used for the suspensions, the size and shape of the mirror, all so as to obtain for the intrinsic constants the values which the general design shows they should have. It also includes devising some of the procedures to be followed in the construction, means for adjusting, a consideration of the general appearance, etc. In case the galvanometer is to be of the moving magnet type, means for astaticizing and shielding against outside magnetic fields, arrangement of soft iron cores, if any are to be used, etc., must also be decided upon.

If materials were available having just the form we should like and having just the properties we should like, the detail design, and also the construction of sensitive galvanometers, would present no special difficulties. However, the materials available are generally not in the most suitable form and are more or less lacking in the properties we should like them to have. The winding, which should be nonmagnetic, is usually slightly magnetic in fairly weak fields and more magnetic in strong fields, the wire available for the winding and for the suspensions has resistance, the magnet steel may not be capable of maintaining the desired field unless the magnet is made larger or the air gap smaller than we should like, the wire of the winding must be insulated and the insulation adds to the mass and takes up valuable space, and even the air damps the motion of the moving system and thus adds to the energy necessary to produce a deflection. If the galvanometer must be especially delicate, much will necessarily depend upon the skill and even the temperament of the person who is to carry out the construction. For these reasons many compromises must be made so that the design may not be so much what is desired as what seems most feasible under the particular circumstances. Such compromises as are made must necessarily be made in such a way as to retain those values for the intrinsic constants given by the general design, except as the general design may be modified to meet better the conditions encountered in the detail design or construction.

Because the materials available may not be in a suitable form or may not have suitable properties, the detail design and construction may present serious difficulties or even be impossible of realization. It is in the avoiding or overcoming of these difficulties that real skill in galvanometer design and construction is shown.

However, the detail design of galvanometers or of any particular galvanometer is not a matter which could properly be considered fully in this paper. In a previous paper[14] a brief detail description is given of a particular type of instrument, and possibly in later papers matters pertaining to detail design and construction may be considered.

IV. SUMMARY

1. Attention is called to the fact that galvanometers are used critically damped or approximately critically damped in four distinct classes of measurements, in each of which the sensitivity with which the user is concerned is with respect to a different quantity. In the first, it is with respect to current in a circuit of high resistance; in the second, it is to voltage in a circuit of fairly low resistance; in the third, it is to current impulse in a circuit containing a condenser; and in the fourth, it is to voltage impulse in a circuit of fairly low resistance.

2. A clear distinction is made between these sensitivities and other operation constants in which the user of the galvanometer may be interested, and the inertia constant, the damping constant, the restoring constant, the dynamic constant, and the resistance, these latter being the construction or intrinsic constants with which the maker of the galvanometer is concerned.

3. It is pointed out that for any one of these classes of work the user is concerned at most with but three operation constants, while the galvanometer has five intrinsic constants. Hence, different values for the intrinsic constants may give identical values for the operation constants; or, in the design of a galvanometer to have particular values for its operation constants, values for some of the intrinsic constants may be chosen arbitrarily.

4. It is shown that in all cases the value for the resistance of a galvanometer may be chosen arbitrarily without interfering in any way with the determination of values for the remaining intrinsic constants such that the galvanometer will have the previously selected or specified values for the set of operation constants pertaining to any one of the four classes of measurements. However, in many cases, unless a fairly low value is chosen, there may be difficulties in carrying out the construction.

5. For galvanometers to be used in the detection or measurement of current in a circuit of high resistance or of current impulse in a circuit containing a condenser, it is shown that in addition to a value for the resistance a value for any other one of the intrinsic constants may also be chosen arbitrarily; and values may be calculated for the other three such as will give previously selected values for the operation constants pertaining to either of these two classes of measurements. This is in case the galvanom-

eter is to be critically damped with the winding open-circuited. In case a shunt is to be used to bring about critical damping, corresponding arbitrary choices in values may be made.

6. For galvanometers to be used in the detection or measurement of voltage or voltage impulse in circuits of fairly low resistance, it is shown that when a value is chosen for the resistance an upper limit for the damping constant may at once be calculated. Choosing a value under this limit, values for the remaining intrinsic constants may readily be calculated to give previously selected or specified values for the operation constants pertaining to either of these two classes of measurements. Attention is called to the fact that the higher the sensitivity and external critical resistance, and the shorter the period desired, the smaller must be the inertia constant and the restoring constant.

7. The detail design of a galvanometer, which consists in deciding upon the size and proportions of the magnet; the size, shape, and number of turns and size of wire for the winding; the size, shape, and kind of material to be used for the suspension, and all such matters, are considered briefly; and it is pointed out that much must necessarily depend upon the properties of the materials available for use in the construction and, especially in case the galvanometer must be delicate, much must also depend upon the skill in manipulation of the person who is to carry out the construction.

This paper relates to a part of a general investigation of galvanometers which is being carried on by the author and Ernest Weibel, who has made valuable suggestions concerning matter discussed here.

WASHINGTON, December 30, 1915.

INTERFERENCE MEASUREMENTS OF WAVE LENGTHS IN THE IRON SPECTRUM (3233A—6750A)

By Keivin Burns, W. F. Meggers and Paul W. Merrill

CONTENTS

Page.
I. Introduction 245
II. The region of the spectrum covered 246
III. Apparatus 246
IV. Source 247
V. The observations 248
VI. Method 248
  1. Standards and corrections 248
  2. Use of three interferometers 249
  3. Reduction 250
VII. Results 250
  1. Use of earlier measurements 250
  2. Character of lines 251
  3. Description of Table 1 251
VIII. Agreement of standards 260
  1. General 260
  2. Standards for which B. S. minus I. A. is greater than 0.001A 260
  3. Unsatisfactory standards 261
  4. Pole effect and interference measurements 261
IX. Comparison with grating measurements 262
  1. General agreement 262
  2. Intensity equation 263
X. Character of certain additional lines 265
  1. Rejected interference observations 265
  2. Tertiary standards 265
XI. Correlation of sharpness with other properties 267
  1. Introduction 267
  2. Pole effect 268
  3. Intensity 270
  4. Behavior under pressure 270
XII. Summary 272

I. INTRODUCTION

The Bureau of Standards took up the matter of standard wave lengths of light over a year ago and a list of such wave lengths was published.[1] In that paper attention was called to the need and demand for such work on account of its importance to astronomers, metrologists, physicists, and chemists. It may be stated that the demand for more accurate wave lengths is increasing. This demand is being made by the theoretical physicist and also by the analytical chemist. Some instances have come to the attention of the Bureau in the past year in which it was difficult or impossible to make an analysis, due to the present imperfect state of wave-length determinations. The first step must be to determine the standards of wave length and it is the purpose of this Bureau to make such determinations as accurately as possible throughout the entire length of spectrum which can be photographed. The present article is a continuation of the work published in the paper to which reference was made above. In that paper the reason for using the iron spectrum was given, the present state of standards was discussed, and the hope of cooperation with other observers was expressed.

---

[1] This Bulletin, 12, p. 179; 1915 (Scientific Paper No. 251).

II. THE REGION OF THE SPECTRUM COVERED

The present paper covers the region 3233A to 6750A (1A = 1 × 10^{-7} mm), the whole range of the international standards. There are too few of these standards for many purposes, so, wherever it was possible, lines were observed at intervals of about 10A; that is, the wave length of each successive line is 10A greater than that of the line preceding. At many points in the iron spectrum it is impossible to find sharp lines of sufficient intensity at such close intervals. In some cases, lines of an unsatisfactory character were measured in these regions and experience may prove that these lines are worthless as standards. No impurity lines were observed. The advisability of using impurity lines to fill gaps in the iron spectrum will be taken up in a later publication. At present we are of the opinion that these lines should be used with circumspection.

III. APPARATUS

The apparatus used was similar to that previously described.[2] The light from the arc was focused on the interferometer by means of a simple quartz lens. The interferometer plates were quartz disks 8 mm in thickness, whose inner surfaces had a semitransparent coating of platinum, cathodically deposited. These plates were kept parallel to each other by means of invar separators. The aperture of the interferometer was limited to 9 mm by a diaphragm. The interference rings were projected upon the slit either by means of a quartz-fluorite lens or by a glass lens which was achromatic throughout the visible spectrum. This latter was designed by Mr. Tillyer and made at the Bureau of Standards. The spectrum was formed by an Anderson concave grating mounted in parallel light. The first order is very bright on one side, and the second on the same side is quite satisfactory in this respect. In the second order the scale is 5A per millimeter; about 900A can be photographed in sharp focus in the second order, and 1800A in the first. The grating was ruled 299 lines per millimeter, there being 39 800 lines in all. Light passing through the slit fell upon a concave mirror, from which it was returned as a parallel beam to the grating placed close beside the slit. The grating was mounted on one end of a webbed steel beam which could be rotated around the axis passing through the center of the grating. The other end of the beam slipped along a double track, thus bringing the different orders of the spectrum to the camera, which was free to slide lengthwise of the beam. When the proper region was reached the camera was clamped firmly to the double track, which was strongly cemented to a solid brick pier. The whole apparatus could be clamped to massive piers, which were all cemented to a thick concrete floor. The stability of the spectroscope apparently leaves nothing to be desired, as the longest exposures were perfectly sharp. On account of the fact that the slit and the center of the grating are 4° apart, as seen from the mirror, there is a slight astigmatism in the image. The focus of the camera was usually set to make the rings sharp. In the first order region, 4900A to 6800A, this procedure broadened the lines too much and a mean focus was used. The peculiar bend in the reduction curve in this region may be connected with this fact.

---

[2] This Bulletin, 12, p. 179; 1915 (Scientific Paper No. 251.)

IV. SOURCE

The source was an arc either of electrolytic iron or of Norway iron, the former being used for at least one plate in each region. The normal conditions recommended by the international wave length committee[3] were rigorously fulfilled. The region 3500A to 4200A was observed with both 4 and 6 amperes, but no differences in wave length were detected as a result of the increased current strength.

---

[3] Kayser et alii, Astroph. J., **39**, p. 93; 1914.

V. THE OBSERVATIONS

Seed 27 plates were used throughout, but to photograph the region 4900A to 6750A the plates were bathed in pinaverdol and dicyanin with ammonia. In the region 3200A to 4200A there were measured: Four exposures of 1; five of 6; one each of 15, 20, and 30; and two of 60 minutes' duration. In the region 3500A to 4500A the exposures were: Five of 2; five of 5; two of 20; and three of 25 minutes. The region 4100A to 5100A was covered by exposures as follows: Three of 3; two of 5; one of 10; four of 15; one of 25; and four of 50 minutes. Finally, in the region 4900A to 6800A, the following exposures were measured: One of 1; two of 3; three of 5; three of 9; two of 15; three of 20; two of 90; and one each of 65, 80, and 100 minutes' duration. The first three regions were photographed in the second order; 4900A to 6800A was taken in the first order. In almost every case two or more exposures were measured on the same plate.

These exposures were made without disturbing the interferometer. In 3 cases out of 24 there was a change in the thickness of about one part in a million, and in a few other cases there was a barely perceptible change. These changes were probably due to a variation in the temperature, although the thermometer beside the interferometer registered no appreciable change. By allowing the light to fall upon the interferometer for half an hour before taking the plate this trouble could be avoided. A short exposure was always made first, and another short exposure usually followed the long one. In any case, each exposure was worked out by itself and this expansion of the interferometer caused no difficulty. In a few cases the long exposure on a plate was too dense to permit of accurate measurement of a sufficient number of standards. In such cases the long and short exposures were tied together by lines of intermediate intensity. It will be seen at once that this method would lead to erroneous results in case there were an intensity equation. The question will be discussed later in connection with the grating observations.

VI. METHOD

1. STANDARDS AND CORRECTIONS

The method of reduction was that of Buisson and Fabry,[4] outlined in the former paper on wave lengths. Since the secondary I. A. standards were used, it is probable that at all points in the spectrum the resulting system is more nearly correct than would have been the case if the fundamental standard had been used. For these standards are the result of three independent series of observations, and in the mean are no doubt very nearly correct. The use of the fundamental standard would have introduced the troublesome question of phase change, and the results would surely have been no more nearly correct than any one of the three original series of observations. Having used the I. A. normals, it is probable that the mean wave length of several lines near any point in the spectrum is very nearly as accurate as the I. A. system at that point. Since the standards were distributed throughout the whole region, no correction to normal temperature and pressure was necessary.

---

[4] Buisson and Fabry, Astroph. (8), 28, (1) p. 169; 1908.

2. USE OF THREE INTERFEROMETERS

In one particular the present investigation departs from the practices of former observers, namely, in the use of at least three interferometers for the observation of each line. This procedure has many advantages. For one thing, some lines can not be observed with a very high order of interference, and in order to measure the wave lengths of these lines one is tempted to use a low order, and so sacrifice the accuracy that might be obtained for other lines in using a thicker interferometer. By using a low, an intermediate, and a high order these poor lines may be measured with some accuracy, and the accuracy of the good lines is no doubt somewhat increased. The wave lengths of the sharp lines were not derived by means of the thickest interferometer alone for the reason that it was considered more important to eliminate the effect of a small error in the determination of the angular diameter of the ring system. The elimination of this error is accomplished by using more than one etalon, since the standards are situated throughout the whole region under observation. In changing from one interferometer to another, care was taken to rotate the plates with respect to each other in order to minimize the effect of slight irregularities in their surfaces. In the case of double lines, the components may be nearly in phase in one interferometer but out of step in another. In this way a few doubles were eliminated. A good illustration is found in 5269.5A. This line gives sharp interference of orders 38 thousand and 57 thousand, but shows two sets of rings of order 28 thousand. The wave lengths of the two components are 5269.495 and

5269.595, the interval being great enough to be seen with a large grating. In a few other cases the wave length determined by one interferometer differed too much from that found by means of another, and the line was discarded on the ground that it might be a close double. Poor lines, of course, could not be observed with the higher orders of interference, and no line which is measured by means of only one interferometer is recommended as a standard where the highest accuracy is involved.

3. REDUCTION

Having 15 to 30 standards on each plate, the thickness of the interferometer was determined from three or more of them and all wave lengths computed. Then all available standards (observed minus I. A.) were represented as closely as possible by a smooth curve. The curve was usually a straight line excepting in the region 4900A–6800A. In this latter region the line was bent at 6100A, and was always straight from 6100A to 6800A. This bend is thought to be due to instrumental causes, yet it may be due in part to inaccuracies in the secondary standards. Having drawn the curve, all wave lengths were corrected by means of it.

VII. RESULTS

1. USE OF EARLIER MEASUREMENTS

In the region 3233A to 3600A all wave lengths which had been published by the Bureau[5] were remeasured by means of at least one interferometer whose thickness differed from that used in the earlier work. If the new wave length did not exactly check the old, the line was completely remeasured. All lines which were poorly determined (marked "C") in the earlier work were completely remeasured; this includes all lines between 3600A and 3701A. The mean of all observations, both the earlier determinations and those made by the writers, was used to form the value found in Table 1. From 5434A to 6750A all lines, formerly measured by Burns,[6] were completely remeasured unless they were too faint on the Bureau plates. Usually the mean of all observations, the early measurements by Burns and those by the writers, was used as the value to be published in Table 1.

---

[5] This Bulletin, 12, p. 179; 1519 (Scientific Paper No. 251).

[6] Burns, Jour. de Phys., 5th series, 3, p. 457; 1913.

However, in some cases the dispersion used by Burns was considered inadequate to separate close pairs sufficiently, and only the observations made at the Bureau were used.

2. CHARACTER OF LINES

The limiting order with which a line can be observed is a direct measure of its sharpness. Further, it is of interest to know that a line has been examined by means of more than one interferometer, as a double may show interference of a high order. Frequently a line will show poor rings in each of several orders, but usually, if a line is poor at a given order, it shows no rings at all when the path difference is increased 30 to 50 per cent. The character of the lines may be judged by an inspection of their behavior under increasing order, the data being found in Table 1. Unless otherwise noted all lines of wave length less than 3960A which are included in the table showed sharp rings in interferometers of 2 mm and 3 mm thickness.

3. DESCRIPTION OF TABLE 1

Column 1 contains the observed wave length at 15° and 760 mm. Column 2 contains the intensity and character of the line as seen by means of a grating, using 6 or 7 amperes. "b" = broad; "d" = double; "h" = hazy; "l" = shaded to red; "r" = narrow reversed; "v" = shaded to violet. Column 3 contains letters which indicate the probable error deduced from the agreement of individual exposures. "A" indicates a probable error less than 0.0007A; "B," 0.0007A to 0.0012A; "C" means that the determination was poor. Column 4 contains the orders of interference in thousands which were used in measuring the wave length, and column 5 contains additional orders at which the lines were examined but not measured. An asterisk (*) indicates that the rings were measurable but not sharp; an exclamation point (!) indicates the absence of interference.[7]

---

[7] We suggest that a laboratory study of the sharpness of lines under varying conditions may be of great assistance in interpreting solar and stellar phenomena, when the sharpness of lines in celestial sources shall have been investigated.

TABLE 1

Wave Lengths and Characters of Iron Lines (3233–6750)

Wave length	I	p. e.	Order Meas.	Order Exam.
3233.056	5	A	23 31	46
36.227	5	A	23 31	46
39.440	8	B	23	18* 31* 46!
44.189	8	B	23	18* 31* 46!
54.367	4	A	23 31	46
57.598	4	B	23 31	46
65.622	6	A	23 31	46!
71.005	6b	A	23 31	46!
80.264	5	A	23 30	46
84.593	4	A	23 30	46
86.760	8	A	23	12* 18* 30!
90.992	4	B	23 30	
3298.136	5	A	23 30	45!
3305.977	8	A	23 30	
06.358	8	A	23 30 45*	
14.746	6	A	23 30	45
23.741	4	A	23 30	45
28.870	4	A	23 30	45
37.670	4	A	22 30	
47.930	4	A	22	30
55.232	4	A	22 30 45	
70.787	6	A	22 29 44	
79.024	4	B	22 29 44	
80.115	5	A	22 29 44	
83.984	5	A	22 29 44	
92.658	5	A	22 29 44	
94.588	4	A	22 29 44	
96.981	3	A	22 29	44
3399.338	6	A	22 29 44	
3401.523	4	A	22 29 44	
02.261	4	A	22 29 44	
07.464	71d	A	22	18* 29!
13.136	7	A	22 29 44	
15.537	4	A	22 29 44	
17.844	6	A	22 29 44	
18.512	5	A	22 29 44	
24.289	6	A	22	29 44!
27.122	6	B	22	29* 44!
28.197	6	A	22 29 44	
31.822	2b	C	22 29	44!
42.366	4	B	22 29 44*	
45.153	4	A	22 29 43	
47.282	6	A	22 29 43	
50.332	6	A	22 29 43	
58.306	3	A	22 29 43	
59.916	4	A	22 29	43*
76.707	5r	A	22	11* 17* 29* 43*
85.343	6	A	21 29 43	
89.673	4	A	21 29 43	
95.292	4v	A	21 29 43	

TABLE 1—Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Meas.	Order Exam.
97.111	4	B	21	29 43*
3497.847	5r	B	21	11* 17* 29* 43*
3506.501	5	A	21 29 43	
13.822	5	A	21	11* 17* 28!
21.266	5r	B	21	11* 17* 28!
27.796	4	B	21 28	42* 57!
29.819	4	B	21 28	42* 57!
36.558	6	A	21	11* 28* 42!
41.089	6h	A	21	11* 17* 28!
42.080	6	A	21	11* 17* 28!
45.642	5	A	21 28	42
54.928	8h	B	21	11* 17* 28!
56.878	6h	A	21	11* 17* 28!
58.519	5r	C	21	11* 17* 28* 42*
60.703	2	A	21 28 42 56*	
71.999	-7h	B	21 28	42!
76.762	4	A	21 28 42 56	
82.203	4	A	21 28 42 56	
86.117	5	A	21 28 42	56!
89.108	4	A	21 28 42 56	
3594.632	5	A	21	28* 42* 56!
3603.207	5	A	21 28 42 56	
06.682	5	A	21 28	42* 55!
10.159	5h	B	21	11* 17* 28!
12.084	4	B	21 28	42* 55!
17.789	6	A	21 28 42	55!
21.464	6	A	21 28 41	55!
22.007	6	B	21 28 41	55*
23.188	5	A	21 28 41 55	
25.150	6	B	21 28	41 55!
32.044	6	A	21 28 41 55	
38.299	6	B	21 28 41	55
40.392	6	A	21 28 41	56*
45.825	4	A	21 27 41	55
51.471	6	A	21 27 41	
59.520	5	A	21 27 41	55
69.524	6	A	20 27 41 55	
76.313	4	A	20 27 41 54	
83.058	4	B	20 27 41*	54!
84.112	5	A	20 27 41	54*
89.458	6	B	20 27	41* 54!
3695.055	3	A	20 27 41 54	
3701.084	6	B	20 27	41* 54!
04.465	5	A	20 27 40 54	
07.050	3h	A	20 27 40*	54!
15.915	2	A	20 27 40 54	
24.380	6	A	20 27 40 54	
31.377	1	A	20 27 40 54	
32.401	6	A	20 27 40	54!
38.308	4	A	20 27 40 54	

TABLE 1—Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Mess.				Order Exam.
44. 101	2h	B	20	27	40*		54!
53. 615	5	A	20	27	40	54	
60. 053	5	A	20	27	40	54	
65. 544	6	A	20	27	40		54!
74. 828	2	A	20	27	40	54	
81. 190	1	A	20	26	40	53	
85. 951	5	B	20	26	40	53	
86. 680	3	A	20	26	40	53	
3794. 342	3	A	20	26	40	53	
3805. 346	6	A	20	26	39		53*
14. 527	2	A	20	26	39	52	
21. 181	6	A	20	26	39		52*
33. 313	4	A	20	26	39	52	
43. 261	5	A	20	26	39	52	
50. 821	5	A	19	26	39*		52!
52. 578	3	A	19	26	39	52	
59. 215	5	A	19	26	39	52	
67. 220	3	A	19	26	39	52	
73. 764	4	A	19	26	39	52	
84. 362	2	A	19	26	39	51	
3891. 932	4	A	19	26	39	51	
3903. 903	3	A	19	26	38	51	
07. 938	3	A	19	26	38	51	
17. 186	5	A	19	25	38	51	
25. 948	3	A	19	25	38	51	
35. 817	4	A	19	25	38	51	
40. 883	4	A	19	25	38	51	
48. 780	4	A	19	25	38	51	
52. 606	4	B	19	25	38	51	
66. 068	5	A	19	25	38	50	
77. 746	5	A	19	25	38	50	
83. 963	5	A	19	25	38	50	
90. 380	1	A	19	25	38	50	
3997. 397	6	A	19	25	38	50	
4009. 718	5	A	19	25	37	50	
14. 536	4	A	19	25	37	50	
21. 872	5	A	19	25	37	50	
31. 966	2	A	19	25	37	50	
41. 298	1	A	19	25	37	49	
44. 616	2	A	19	25	37	49	
62. 448	4	A	18	25	37	49	
66. 980	4	A		25	37	49	
74. 792	3	A		25	37	49	
85. 010	2	A		24	37	49	
4095. 977	3	A		24	37	49	
4107. 494	5	A		24	36	49	
18. 551	6	A		24	36	49	
27. 614	4	A		24	36	48	
34. 684	5	A		24	36	48	
43. 420	5	A		24	36	48	

TABLE 1—Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Meas.			Order Exam.
47.675	4	A	24	36	48	
56.804	4	A	24	36	48	
70.908	2	A	24	36	48	
75.642	4	A	24	36	48	
81.760	6	A	24	36	48	
4191.446	6	C	24	36*		48 !
4203.989	3	A		36	48	
13.653	2	A	24	35	47	
16.188	4	A	24	35	47	
22.227	5	B	24	35		47 !
45.261	2	A	24	35	47	
67.834	2	A	23	35	47	
68.758	2	C	23	35	47	
82.408	6	A	23	35	47	
91.469	1	A	23	35	47	
4298.042	2	A	23	35	47	
4309.379	2	A	23	35	46	
15.090	5	A	23	35	46	
27.100	2	A	23	35	46	
37.052	5	A	23	35	46	
52.740	4	A	23	34	46	
58.507	2	A	23	34	46	
67.583	2	A	23	34	46	
69.777	3	A	23	34	46	
75.935	5	A	23	34	46	
87.898	2	A	23	34	46	
4390.956	3	A	23	34	46	
4408.421	4	A	23	34	45	
22.573	4	A	23	34	45	
27.315	5	A	23	34	45	
30.622	4	A	23	34	45	
35.154	2	A	23	34	45	
42.346	5	A	23	34	45	
43.199	3	A	23	34	45	
47.725	5	A	23	34	45	
54.386	3	A	22	34	45	
59.125	5	A	22	34	45	
61.658	4	A	22	34	45	
66.556	5	A	22	34	45	
76.023	7	A	22	34	45	
84.234	3	A	22	33	45	
4494.571	5	A	22	33	45	
4514.192	2	A	22	33	44	
17.530	2	A	22	33	44	
28.622	7	B	22	33		44 !
31.154	5	A	22	33	44	
47.853	3	A	22	33	44	
52.546	2	B	22	33	44	
74.725	2	B	22	33	44	
81.526	2	B	22	33	44*	

TABLE 1—Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Meas.	Order Exam.
87. 135	2	B	22 33 44	
92. 656	4	A	22 33 44	
4595. 364	2	B	22 33 44	
4602. 007	2	B	22 33 43	
02. 946	4	A	22 33 43	
07. 663	4	B	22 33 43	
13. 221	3	A	22 33 43	
19. 299	4	A	22 32 43	
25. 061	4	A	22 32 43	
30. 128	3	A	22 32 43	
32. 917	3	A	22 32 43	
37. 519	4	A	22 32 43	
47. 439	4	A	22 32 43	
67. 461	4	A	21 32 43	
68. 152	4	A	21 32 43	
78. 857	5	A	21 32 43	
4691. 417	4	A	21 32 43	
4707. 289	5	A	21 32 42	
10. 288	3	A	21 32 42	
33. 597	3	A	21 32 42	
35. 849	2	A	21 32 42	
36. 790	5	A	21 32 42	
41. 535	3	A	21 32 42	
57. 585	2	B	21 32 42	
72. 820	3	A	21 31 42	
86. 812	3	A	21 31 42	
88. 763	2	A	21 31 42	
4789. 657	3	A	21 31 42	
4802. 887	2	B	21 31 42	
39. 551	2	B	21 31 41	
59. 756	5	B	21 31 41	
71. 333	8	A	21 31 41	
72. 154	6	A	21 31 41	
78. 227	5	A	20 31 41	
4890. 771	7	B	20 31 41	
4903. 326	5	A	20 31 41	61 !
19. 009	8	A	20 31 41	61 !
24. 777	3	A	20 30 41	61 !
38. 828	5	A	20 30 41	61 !
39. 691	3	A	20 30 41	61
46. 403	2	A	20 30 40	61 !
66. 106	5	A	20 30 40	60 !
73. 116	2	A	20 30 40	60 !
78. 617	2	A	20 30 40	60 !
4994. 133	3	A	20 30 40	60
5001. 879	5	A	20 30 40	60 !
12. 072	4	A	20 30 40	60
14. 958	4	A	20 30 40	60
22. 250	4	A	20 30 40	60 !
28. 130	2	A	20 30 40	60

TABLE 1—Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Meas.			Order Exam.	
41.076	3	A	20	30	40	59	
41.759	4	A	20	30	40	59	
49.827	5	A	20	30	40	59	
51.638	4	A	20	30	40	59	
68.782	4	A	20	30	39	59 !	
83.343	4	A	20	30	39	59	
5098.709	4	C		29	39	20	59
5110.414	4	A	20	29	39	59	
23.724	4	A	20	29	39	59	
27.364	3	A	20	29	39	58	
31.473	2	A	19	29	39	58	
41.745	2	A	19	29	39	58	
50.844	4	A	19	29	39	58	
51.914	3	A	19	29	39	58	
66.285	3	A	19	29	39	58	
67.495	8	C		29	39	19	58 !
71.600	7	A	19	29	39		58
91.471	7	A	19	29	38	58	
92.362	8	A	19	29	38	58 !	
5198.716	4	A	19	29	38	58	
5202.340	5	A	19	29	38	58	
08.609	4	A	19	29	38	58	
16.278	5	A	19	29	38	57	
25.529	2	A	19	29	38	57	
32.957	8	A	19	29	38	57 !	
35.395	2	A	19	29	38	57	
42.496	3	A	19	29	38	57	
50.651	3	A	19	29	38	57	
63.321	5	A	19	28	38	57*	
66.572	8	A	19	28	38	57 !	
70.360	8	C		28	38	19	57 !
81.807	5	A	19	28	38	57*	
5283.636	7	A	19	28	38	57*	
5302.315	5	A	19	28	38	57 !	
07.364	2	B	19	28	38	57	
22.047	2	C	19	28	38	56 !	
24.195	6	A	19	28	38	56 !	
28.538	4	B		28	38	19	56*
32.902	2	A	19	28	38	56	
41.027	5	A	19	28	37	56	
53.385	2	A	19	28	37	56 !	
65.403	2	A	19	28	37	56	
71.497	7	C		28		19	37 !
79.579	2	A	19	28	37		56
93.183	4	A	19	28	37	56 !	
5397.132	6	A	19	28	37	56 !	
5405.781	6	A	19	28	37	55 !	
29.701	6	A	18	28	37	55 !	
34.528	6	A	18	28	37	55	
46.920	6	A	18	28	37	55 !	

TABLE 1—Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Meas.			Order Exam.		
55. 614	6	A	18	27	37	55!		
73. 913	3	A	18	27	37	55!		
5497. 521	4	A	18	27	37	55		
5501. 468	4	A	18	27	37	54		
06. 783	4	A	18	27	37	54		
25. 557	2	B	18	27	37	54!		
35. 423	2	B	18	27	37	54!		
43. 184	2	C	18	27	37	54!		
43. 953	2	B	18	27	37	54!		
63. 611	3	B	18	27	37	54!		
69. 633	5	A	18	27	37	54*		
72. 859	5	A	18	27	37	54*		
76. 106	4	A	18	27	37	54*		
5586. 772	6	A	18	27	36	54*		
5615. 661	6	B	18	27	36	53!		
18. 646	1	B	18	27	36			
24. 559	5	B	18	27	36	53*		
38. 276	3	A	18	27	35	53!		
41. 458	2	C	18			27	35*	53!
55. 505	2	C	18			27*	35!	
58. 835	4	B	18	26	35	53*		
62. 534	3	A	18	26	35	53!		
5693. 638	2	B	18	26	35			
5701. 553	3	A	18	26	35	53*		
09. 395	3	A	17	26	35	53*		
17. 853	3	B	17	26	35	52!		
31. 774	3	B	17	26	35			
41. 865	2	C	17			26	35!	
53. 142	3	A	17	26	35	52*		
63. 013	4	A	17	26	35	52*		
75. 099	3	B	17	26	35	52*		
91. 045	2	B	17	26	34			
93. 936	2	C	17	26		34!		
5798. 198	2	C	17	26	34			
5862. 348	4b	C	17			26!		
5883. 842	4	C	17			26*	34*	
5905. 682	2	C	17			25*	34*	51!
16. 252	3	B	17	25	34	51!		
34. 681	4	B	17	25	34	50!		
75. 352	2	A	17	25	33			
5976. 804	2	B	17	25	33			
6003. 037	3	B	17	25	33			
08. 582	3	B	17	25	33			
27. 059	2	A	17	25	33			
42. 092	2	A	17	25	33			
55. 990	3h	B	17			25*	33!	
65. 492	4	A	16	25	33	49		
78. 484	3	B	16			25*		
6089. 570	1	B	16	25				
6102. 185	3	C	16	24*		33!		

TABLE 1—Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Meas.			Order Exam.	
27.914	2	A	16	24	33		
36.625	4	A	16	24	33	49	
37.700	4	A	16	24	33	49	
41.758		B	16	24	33		
51.632	2	C		24	32	16	
57.736	2	B	16	24	32		
65.370	2	B	16		32		
70.495	2b	C	16			24*	32!
73.344	2	B	16	24	32		
6191.569	5	A	16	24	32	49	
6200.323	2	A	16	24	32		
13.440	3	A	16	24	32	48	
15.152	2	B	16	24	32		
19.290	3	A	16	24	32	48	
30.734	5	A	16	24	32	48	
32.667	2	A	16	24	32		
40.660	2	B	16	24	32		
46.340	4	A	16	24	32	48*	
52.567	4	A	16	24	32	48	
54.266	3	A	16	24	32	48	
56.372	3	A	16	24	32	48	
65.143	3	A	16	24	32	48	
70.236	2	C		24	32	16	
80.625	2	A	16	24	32		
6297.802	3	B	16	24	32	48	
6301.524	5	B	16	24	32	48	
02.515	3	B	16	24	32	48	
18.028	4	A	16	24	32	47	
22.697	3	A	16	24	32		
35.342	4	A	16	24	32	47	
36.846	4	A	16	24	32	47	
44.159	2	B	16	24	32		
55.042	3	B	16	24	31		
80.753	3	B	16	23	31		
6393.612	5	A	16	23	31	47	
6400.027	5	A	16	23	31	47*	
6408.044	4	B	16	23	31	47	
11.674	5	A	16	23	31	47	
21.360	4	A	16	23	31	47	
30.857	5	A	16	23	31	47	
62.737	4	A	15	23	31		
75.639	3	C	15	23	31		
81.882	3	A	15	23	31		
6494.994	5	A	15	23	31	46	
6518.382	3	B	15	23	31		
46.253	5	A	15	23	31	46	

TABLE 1— Continued

Wave Lengths and Characters of Iron Lines (3233–6750)—Continued

Wave length	I	p. e.	Order Meas.	Order Exam.
75.029	3	A	15 23 30	
92.926	5	A	15 23 30	46
6593.884	3	C	15 23 30	46
6609.125	4	A	15 23 30	
63.454	4	A	15 22 30	45
6678.000	5	A	15 22 30	45
6750.164	4	B	15 22 30	44

NOTES TO TABLE 1.—OTHER INTERFERENCE OBSERVATIONS

3271. Buisson and Fabry,[1] 0.003; Pfund,[2] 0.008.

3323. Buisson and Fabry, 0.739; Pfund, 0.738.

3536. This wave length may have been affected by a neighboring line.

4678. Buisson and Fabry, 0.855.

5127. Buisson and Fabry, 0.364.

5535. Buisson and Fabry, 0.418.

5934. Buisson and Fabry, 0.683.

6003. Buisson and Fabry, 0.039; Eversheim,[3] 0.039.

6127. The value formerly obtained by one of us, 0.919, was not used in taking the mean on account of the large discrepancy.

6663. Eversheim, 0.449.

---

[1] See note 4, p. 248. [2] Unpublished. [3] Eversheim, Annal. der Phys., 4th series, 45, p. 454; 1914.

VIII. AGREEMENT OF STANDARDS

1. GENERAL

The fact that for 15 standards the difference, Bureau of Standards minus International, could be reasonably well represented by a straight line permits a determination of the relative accuracy of the individual I. A. standards.[8]

2. STANDARDS FOR WHICH B. S.–I. A. IS GREATER THAN 0.001A

Eighty-one standards were measured. Expressed in 0.001A, the differences B. S. minus I. A. are as follows: 0, 27; ±1, 35; ±2, 12; ±3, 5; ±4, 2. The following table contains all standards for which this difference is over 0.001A. Differences of 0.002A are to be expected occasionally, as the probable error of the standard is sometimes quite large. In Table 2 the first column contains the B. S. value; the second, the I. A.; the third, some recent determinations by Eversheim[9]; and the last column contains the p. e. of the standard.

---

[8] Kayser et alii, Astroph. J., 32, p. 215, 1909; and 39, p. 93, 1914. [9] See note 3, this page.

TABLE 2

Standards Differing by More than 0.001A from I. A. Values

Wave lengths	I. A.	E.	p. e.	Wave lengths	I. A.	E.	p. e.
3370.787	789		0.6	5001.879	881		1.4
3485.343	345		.6	5167.495	492		.8
3556.878	881		1.0	5266.572	569		.2
4191.446	443		1.0	5371.497	495		1.2
4592.656	658		.2	6265.143	145	145	1.7
4736.790	786		.6	6430.857	859	856	1.4
4859.756	758		.6	6546.253	250	250	1.2
4878.227	225		.4	6592.926	928	920	1.2
4919.009	007		.4	6678.000	004	997	1.6
4966.106	104		.4				

NOTES TO TABLE 2

3556 and 4191 are poor lines which could be measured only with a small order of interference. They had little weight in the final results.

The B. S. value of 5167 is poorly determined, being marked "C" it is not meant as a definitive wave length.

5266 was measured on 15 exposures, only 5 of which gave values less than 0.572.

4736 and 6678 had no weight in the reductions. It is to be noted that Eversheim's most recent determination is more in accord with B. S. value than was his value which entered into the mean which is published as I. A.

6546.247 was used by the international committee as one of three observations, the mean of which is the I. A. wave length. This is a typographical error. The correct value is 6546.254, and the resulting mean is 0.252, which causes the discrepancy B. S. minus I. A. to vanish in the case of this line.

3. UNSATISFACTORY STANDARDS

The line 3677 was measured on all the plates used in this region, yet it was excluded from Table 1 on account of the large discrepancies found in the values obtained for it. The following lines are too poor on all of our plates: 3865, 3906, 4076, 4233. The following standards are lacking in sharpness compared with other lines in their neighborhoods: 3513, 3556, 3850, 4191, 5371.

4. POLE EFFECT AND INTERFERENCE MEASUREMENTS

Between 4707 and 5324, inclusive, and between 5569 and 5763, inclusive, the greater part of the standards have been found by St. John and Babcock[10] to have longer wave lengths at the pole than in the center of the arc. Now, the standard wave lengths were not observed under normal conditions and the present series was observed under the conditions specified by the international committee. So if, when measured by interference, these lines were displaced by the change in conditions, we should have a break in our reduction curve at 4700A, also at 5350A, 5510A, and 5800A. There being no standards between 5763A and 6027A, it is impossible to say whether or not a break occurs at 5800A. It is very evident that no break of over 0.001A occurs at any of the other points, in fact, there is no evidence of any break at all. This leads us to suppose that such interference observations as have been made give consistent results, regardless of the character of the lines in reference to pole shift. It is to be remembered that the interferometer uses a small portion of the center of the arc, where Goos[11] and St. John and Babcock agree that shifts are not to be feared. Thus it seems probable that the measurement of additional lines on the plates from which the I. A. standards were obtained would lead to the same values of the wave lengths as though the plates had been taken under normal conditions. It follows that an enormous amount of valuable data might be obtained from these plates at the expense of a relatively small amount of labor. It is to be hoped that the spectroscopists who cooperated in the determination of the I. A. standards may be induced to measure a large number of additional lines on the plates which were used in this determination.

---

[10] St. John and Babcock, Astroph. J., 42, p. 231; 1915.

IX. COMPARISON WITH GRATING MEASUREMENTS

1. GENERAL AGREEMENT

The wave lengths given in Table 1 were compared with all series of grating measurement of the iron spectrum which have been made on the I. A. system. The results of this comparison are given for the benefit of anyone who may wish to use the grating determinations to fill in gaps in the series determined by means of the interferometer. The recent measurements of Goos,[12] 3370A to 4233A, are very consistent with the interferometer values, the mean difference Goos minus B. S. being 0.0017A. The older work of Goos[13] was done with a different instrument and the agreement with Table 1 is not good to the red of 4400A. The work of Janicki,[14] 4282A to 4903A, is in excellent agreement with the B. S. values, the mean difference Janicki minus B. S. being 0.0015A. Aside from the lines for which the values observed on Mount Wilson differ from those found at Pasadena, the wave lengths of St. John and Ware[15] (4127A to 6494A) are also in close agreement with the Bureau results. The mean difference St. John and Ware minus B. S. is about 0.0016A. The work of Viefhaus[16] is not in agreement with the B. S. results for wave lengths shorter than 3800A, and not in very good agreement for the lines of greater wave length. The tables of Burns[17] extend throughout the entire region under consideration and these values are in fair agreement with the B. S. system throughout, the mean difference Burns minus B. S. being 0.0019.

---

[11] Goos, Zs. f. wiss. Phot., **12**, p. 259; 1913.

[12] Goos, Astron. Nach., **199**, p. 31; 1914.

[13] Goos, Zs. f. wiss. Phot., **11**, pp. 1, 305; 1912.

[14] Janicki, Zs. f. wiss. Phot., **18**, 173; 1913.

[15] St. John and Ware, Astroph. J., **36**, p. 14, 1912; **38**, p. 5, 1913.

The differences, Grating minus B. S., were taken for each series and these data were collected for each 200A. In 5 out of these 13 regions the algebraic means for the best grating measurements agreed in showing a difference between the B. S. and the grating scale. This is no doubt due in part to an accumulation of errors of like sign in the B. S. table, and in part to the fact that the grating follows the local standards much more closely than does the interferometer. Further, the grating observers used some manganese standards and some iron standards which were too poor to be observed on our plates. The greatest difference is 0.0019A in the region 6200A to 6400A.

The arc has been used under normal conditions in only a comparatively small part of the grating work that has been done to date, and eventually the work will be repeated, observing under normal conditions. Further, there will eventually be other interference measurements of the greater part of the lines contained in Table 1, and the means will be taken to establish I. A. standards. For these reasons the correction of the grating observations so as to make them fit the B. S. scale does not seem to be justified at present. And, for about one-third of the spectrum, the mean of the grating observations without correction would not make the individual lines agree much better with the interferometer work. If it is desired to fill a gap in Table 1 with a wave length which is fairly consistent with the B. S. scale, it seems best at present, all things considered, to take the value from any one of the grating series for which the mean value of Grating minus B. S. is less than 0.002A.

2. INTENSITY EQUATION

By this is meant any difference in wave length which is a function of the intensity of the line. It is illustrated by the differences St. John and Ware minus Burns in the region 5200A to

---

[16] Viefhaus, Zs. f. wiss. Phot., **18**, pp. 209, 245; 1914.

[17] Burns, Lick Obs. Bulletin, **8**, p. 27; 1913.

5400A. The mean difference of six lines of intensity two and three is +0.0035A, all differences being plus; the mean for eight lines of intensity four and five is −0.0004, the differences being zero, positive, and negative; finally, the mean difference for six lines of intensity greater than five is +0.0002, the differences again being zero, positive, and negative. It is plain that in this region the wave lengths of faint lines are systematically greater as measured by St. John and Ware than as measured by Burns. This effect is often seen in the comparison of the results from two grating plates of long exposure, particularly if there has been a change of temperature during either exposure. It may also result from slight errors in the adjustment of the grating, or from the use of an imperfect grating. If such an equation is found, only lines of the same intensity as the standards can be measured with the highest precision. Consequently the most careful examination for this phenomenon was made in connection with the interference observations. Only one plate showed any certain evidence of it.

On the other hand, comparison with the best series of grating observations showed this effect in every case. That the fault did not lie with the interferometer seems evident from the fact that in only one limited extent of spectrum were the different series of grating observations all in accord. The differences, Grating minus B. S., were collected into three groups with reference to the intensity of the lines; faint, moderate, and strong. Then the mean difference for the moderate lines was subtracted from that for the faint lines, and the mean difference for the strong lines was subtracted from that for the moderate lines. For one excellent series of observations this procedure gave positive results throughout the whole spectrum; that is, the grating obtained a longer wave length for the faint lines. In the case of another series of grating observations the opposite was true for the greater part of the spectrum. Thus, the comparison with grating measurements tends to strengthen the view that the interferometer wave lengths are comparatively unaffected by any intensity equation.

X. CHARACTER OF CERTAIN ADDITIONAL LINES

1. REJECTED INTERFERENCE OBSERVATIONS

The following lines, formerly observed by one of us[18] by the interference method, were omitted from Table 1 for various reasons. In Table 3 "p" indicates that the values determined from individual plates were too discordant; "l. w.," low weight, indicates insufficient observations; "d" means double; "f" means faint; and "b" indicates that the rings lacked sharpness.

TABLE 3

Rejected Interference Observations

Wave length	Notes	Wave length	Notes	Wave length	Notes
3443	d	5602	([a])	5984	b, p
3468	d	5712	f	6020	([a])
5436	f, p	5714	f	6358	([b])
5483	b, p	5809	p	6569	b, l. w.
5567	f, p	5952	p		
5598	b, l. w.	5956	p		

[a] There is another line too close to 5602 and 6020.

[b] The poor agreement from one interferometer to another suggests a satellite in the case of 6358.

2. TERTIARY STANDARDS

In Table 4 is found a list of those lines which have been suggested for tertiary standards by two or more investigators, and which have not been observed by interference. Column 1 contains the wave length as measured by Burns.[19] For reasons stated above, the wave lengths were selected from one of the series of grating observations, and that of Burns was chosen on account of its being the only one which includes all of the lines. Column 2 gives the intensity and character of each line; R = broad reversal; for other symbols see description of Table 1. Column 3 indicates the order of interference in thousands which these lines show on the Bureau plates. As in Table 1, the asterisk (*) indicates that the rings were poor, and the exclamation point (!) shows lack of interference. With rare exceptions, these lines are less sharp, and therefore, no doubt, less suitable for standards, than other lines in their neighborhood which have already been measured by interference methods.

---

[18] See notes 5 and 6, p. 250.

[19] See note 17, p. 263.

TABLE 4

Character of Certain Suggested Standards

Wave lengths	I	Order				Wave lengths	I	Order			
3372.081	3	22	30	44*		95.004	6r	11*	20!		
78.682	4	22	30			97.516	5	20	26	40	53
87.410	4	22	30	44		98.512	6r	11*	20*	26!	
3406.807	4	22	29	44		99.548	6r	11*	20!		
10.175	2	22	29	44		3806.702	6	20	26	39	53*
25.021	4	22	29	44		08.732	2	20	26	39	53
31.827	2b	22	29			15.844	7R	11!			
37.958	2	22	29			20.430	8R	10!			
40.614	7R	12!				25.886	8R	10!			
40.992	6R	12!				27.826	6R	10!			
51.920	6	22	29	43		34.227	7R	10!			
52.279	4	22	29	43		40.443	6R	10!			
65.864	6R		12!			41.052	6R	10!			
69.012	2	22	29			46.806	5	20	26	39	52*
69.834	2	22	29	43*		56.373	6R	10!			
74.436	2	22	29	43!		59.913	7R	10!			
77.850	2	22	29			65.526	6r	10*	19*	26!	
78.623	2	22	29			72.506	6r	10*	19*	26!	
83.012	4	21	29	43*		78.024	6r	10*	19*	26!	
90.577	6R	12!				83.288	2	19	26	39	51
3500.570	2	21	28	43		86.287	7R	10!			
04.866	2	21	28	43!		88.520	7b	19*	26!		
05.065	2	21	28	43		95.659	5r	10*	19!		
08.492	4v, d	21	28*	43!		97.892	4	19	26	38	51*
10.443	2	21	28	43*		98.013	4	19	26	38	51*
33.004	4	21	28	43*		99.711	6r	10*	19!		
33.196	5	21	28	43*		3902.950	7r	10*	19!		
49.873	3	21	28	42	56*	06.484	5r	10*	19*	26*	
52.840	4h	21	28*	42!		13.635	2	19	26	38	51
67.045	4h	21	28	42!		20.261	6r	10*	19!		
70.102	7R	11!				22.917	6R	10!			
81.197	8R	11!				25.650	2	19	26	38	51
82.202	4	21	28	42	56*	30.304	7R	10!			
87.749	2b	21	28	42!		32.635	3	19	25	38	51
89.453	3	21	28	42	56*	42.446	3	19	25	38	51
99.628	3	21	28	42	56!	49.956	4	19	25	38	51
3602.515	2v	21*	28!			51.165	4	19	25	38	51
08.860	6R	11!				56.461	4	19	25	38	51
31.464	6R	11!				56.682	6	19	25	38	51
47.845	6R	11!				67.426	4	19	25	38	50
55.470	4	21	27	41	55*	69.263	7r	10!			
67.280	4h	20	27*	41!		71.328	4	19	25	38	50
74.768	2	20	27	41	54*	81.776	3	19	25	38	50
78.862	2	20	27	41	54	86.178	3	19	25	38	50
85.995	5h	20	27*	41!		95.989	1	19	25	38	50
97.496	2h	20	27*	41!		98.059	5	19	25	38	50
3711.227	2	20	27	40	54	4005.250	7b	10*	19*	25!	
11.408	1	20	27	40	54	07.233	1	19	25	37	50
19.938	8R	11!				17.154	3	19	25	37	50
22.565	6R	11!				24.745	2	19	25*	37!	
26.922	3h	20	27	40!		32.636	1	19	25	37	49
27.095	2	20	27	40!		45.822	8R	10!			
30.390	3	20	27	40	53*	63.604	8R	10!			
34.869	9R	11!				67.279	3	18	25	37	49!
37.135	7R	11!				76.641	5	18	24*	37!	
3742.623	1h	20	27	40*	53!	78.362	3	18	24	37	49
46.927	2h	20	27*	40!		79.847	2	18	24	37	49
48.264	6R	11!				84.508	4	18	24	37	49!
49.487	8R	11!				98.189	3	18	24	37!	
58.234	7R	11!				4109.810	4	18	24	37	49
63.792	6R	11!				14.454	4		24	37	49
67.194	6R	11!				21.809	2		24	36	49
76.456	2	20	26	40	53	32.064	7		24*	36!	
87.880	6R	11!				37.002	3		24	36	48
90.094	4	20	26	40	53!	43.874	7		24*	36!	

TABLE 4—Continued

Character of Certain Suggested Standards—Continued

Wave lengths	I	Order				Wave lengths	I	Order			
54.504	4		24	36	48	45.804	3b	21	32	42*	
72.748	2		24	36	48	4881.722	2	20	31	41	
77.598	2		24	36	48	85.443	2	20	31	41	
84.894	4		24	36	48	91.510	9	20	31	41	
87.052	6		24	36*	48!	4910.032	2	20	31	41*	
87.812	6		24	36*	48!	20.521	10	20	30*	41!	
91.446	6		24	36	48!	57.311	7	20	30*	40!	
98.314	6		24	36*	48!	57.612	10	20	30*	40!	
99.098	6		24	36	48*	82.524	4b	20	30*	40!	
4202.032	7r		24!			85.267	3	20	30	40	
10.362	6		24	36*	47!	85.562	3	20	30	40	
19.364	5		24	35	47	5005.729	4	20	30	40	
24.172	3b		24	35*	47!	06.134	5	20	30	40	
25.464	4b		24	35*	47!	74.750	2b		30!		
27.445	7		24*	35*	47!	79.228	3	20	29	39	
33.614	6		24	35*	47!	79.742	3	20	29	39	
47.440	5b		24	35*	47!	5107.454	3	20	29	39	59
50.134	7		24	35*	47!	07.645	4	20	29	39	59
50.791	8		24	35*	47!	39.269	6	19	29	39	58
60.489	10		23*	35!		39.481	8	19	29	39	58
71.171	7		23	35*	47!	42.934	3	19	29	39	58
71.764	8r		23*	35!		94.950	5	19	29	39	58
94.132	6		23	35*	47!	5215.195	4	19	29	38	57*
99.254	7		23	35*	47!	17.405	4	19	29	38	57!
4307.910	8r		23*	35!		26.876	5	19	29	38	57!
25.770	9r		23*	35!		27.187	8	19	29	38	57!
67.910	1		23	34	46	29.84	2	19	29	38*	57!
83.548	10R		23!			73.178	3	19	28	38*	57!
88.422	2b		23*	34!		73.379	2	19	28	38	57
4404.752	8r		23*	34!		5328.044	7	19	28*	38!	
07.716	2		23	34	45	39.949	3	19	28	37*	56!
15.127	8r		23*	34!		64.859	3h	19*	28!		
69.390	4b		22*	34!		71.496	7	19	28*	37!	
82.176	3		22	33	45	5400.504	2b	18	28*	37!	
82.262	4		22	33	45	45.040	2h	18	28*	37!	
89.744	3		22	33	45	62.964	2b	18*	28!		
4490.088	2	22	33	44		63.27	4b	18*	28!		
4525.154	3b	22	33	44		76.296	2	18	27	36	55!
56.128	3	22	33	44*		5602.965	3	18	27	36*	
98.138	2b	22	33	44*		5712.150	2	17	26	35*	
4611.290	4b	22	33	43*		14.155	1	17	26	35	
38.020	4	22	32	43*		5809.249	2	17	26	34	
54.502	4	21	32	43		5952.749	4	17	25	34*	
54.637	3b	21	32	43		6020.177	21	16	25*	33!	
73.171	3	21	32	43*		89.567	1		25	33	
83.566	2	21	32	43		6103.196	2h	16	25	33!	
4727.410	2d	21	32	42*		6569.233	5h	15	23*	30!	

XI. CORRELATION OF SHARPNESS WITH OTHER PROPERTIES

1. INTRODUCTION

Five hundred and thirty of the lines contained in Tables 1 and 4 were examined at various orders of interference and were either found to be sharp enough to stand a high order of interference, or their limiting orders were determined. Forty-nine additional lines, all of which are easily reversed, were found to show no interference, even at an order of about 10 000. These lines and about 50 others for which the data were incomplete do not enter into the discussion which follows. The lines examined were arbitrarily divided into four groups. In the first group interference ceased to be visible when the path difference was from 20 000 to 30 000 waves; in the second group, 30 000 to 40 000; in the third group, 40 000 to 60 000; and the fourth group contains the lines still showing interference with the largest path differences observed. The last group is not entirely homogeneous. All the lines in this group show interference with an order of more than 40 000 waves. Some of them would probably have been found to be limited by 60 000 if they had been examined that far, but most of them would possess a limiting order in excess of 60 000 waves because they still show perfect interference between 40 000 and 60 000. The groups are distinct enough to justify some general conclusions when correlated with other data. The material contained in Tables 1 and 4 is incomplete, but so far as it goes it points to the conclusion that the limiting order of the average iron line is independent of the wave length. Fundamentally, we have to do with vibration frequency, and the above shows that the variation from the mean is the same proportion of the frequency for lines in all parts of the spectrum. Or putting it another way, the width of the average line, expressed as a proportion of the wave length, is constant throughout the spectrum; expressed in angstroms, the width is a direct function of the wave length.

TABLE 5

Percentage of Lines in Each Group

Group..............	I	II	III	IV
Limiting order.....	20 000 to 30 000	30 000 to 40 000	40 000 to 60 000	Above the largest observed
Number of lines....	39	48	102	341
Per cent of total lines	7	9	19	65

2. POLE EFFECT

A correlation of these data with those of St. John and Babcock[20] on "Pole effect" is represented in Table 6. Pole effect indicates a change in wave length when the light is taken from the negative pole instead of the center of the arc. Positive shifts indicate increased wave lengths from the negative pole as compared with the center and negative shifts are displacements toward shorter wave lengths.

---

[20] See note 10, p. 261.

TABLE 6

Sharpness and Pole Effect

Group	I	II	III	IV	Totals
Number of positive shifts	6	25	41	35	107
Per cent of positive shifts	6	22	39	33	100
Number of negative shifts	12	6	6	0	24
Per cent of negative shifts	50	25	25	0	100
Positive shifts <.010A	4	6	3	1	14
Positive shifts .010–.015A	1	13	6	14	34
Positive shifts .015–.020A	1	2	12	13	28
Positive shifts >.020A	0	4	20	7	31
Negative shifts <.010A	1	3	4	0	8
Negative shifts .010–.015A	4	1	2	0	7
Negative shifts .015–.020A	4	0	0	0	4
Negative shifts >.020A	3	2	0	0	5

About 19 per cent of the lines examined have positive shifts and a little over 4 per cent have negative shifts. It is interesting to observe that the majority of positive shifts occur with lines which are known to be sharp in the center of the arc because they show interference of rather a high order, while the negative shifts occur principally with poorer lines. Negative shifts are entirely absent from group IV and only a few small ones (less than 0.015A) are found in group III. Positive shifts are mostly larger than 0.015A and occur most frequently in groups III and IV.

Pole shifts of positive sign were obtained by St. John and Babcock from classes "c5" and "d" of the Gale and Adams [21] classification of lines. Large pressure displacements are indicated by "c" and "d," and "5" means unsymmetrical widening toward the red. Negative shifts affect lines which St. John and Ware [22] have placed in a separate class, "e," because they are widened unsymmetrically toward the violet by pressure, and greatly displaced in this direction.

No satisfactory explanation of this pole effect can be given at the present time. Fortunately it may be excluded by using only the center of the arc, as recommended by the international committee.

---

[21] Gale and Adams, Astroph. J., **35**, p. 10; 1912.

[22] See note 15, p. 262.

3. INTENSITY

An attempt was made to connect limiting order and pole effect with intensity. The data are arranged in Table 7.

TABLE 7

Sharpness, Intensity, and Pole Effect

Intensity	1	2	3	4	5	6	7	8	9	10
Number of lines	10	103	94	130	92	60	21	16	1	3
Number of lines, Group I	0	11	6	6	6	2	5	2	0	1
Number of lines, Group II	1	11	8	6	2	8	9	1	1	2
Number of lines, Group III	0	13	15	24	18	21	2	9	0	0
Number of lines, Group IV	9	68	65	94	66	39	5	4	0	0
Per cent of lines, Group IV	90	66	69	72	71	48	24	25	0	0
Number of pole shifts	0	23	22	28	23	13	7	6	1	3
Per cent of lines affected	0	22	23	22	25	22	33	38	100	100
Number of positive shifts	0	15	14	24	21	12	7	5	1	3
Number of negative shifts	0	8	8	4	2	1	0	1	0	0

Broadly speaking, it is seen that limiting order is an inverse function of intensity, and that the frequency of positive shifts tends to increase with large intensities. About 68 per cent of the lines included by intensities 1 to 6 still show interference of an order greater than 40 000, against only 22 per cent of the lines of greater intensity. On the other hand, only 24 per cent of the lines of intensity 1 to 6, inclusive, have pole shifts against 41 per cent of the more intense lines. Lines of small intensity are more frequently affected by negative pole shifts, taking into account only lines in this list.

St. John and Babcock examined 1570 iron lines between 2979 and 6678 and found 23 per cent of the lines affected by pole effect. Among our 530 lines there are 131 affected lines, or about 24 per cent, so that the lines chosen or suggested as standards appear to be representative as far as pole effect is concerned. Inasmuch as practically all the lines in our lists were examined for pole effect, the conclusions drawn from these tables will probably be valid generalizations.

4. BEHAVIOR UNDER PRESSURE

The data on limiting order were also correlated as far as possible with the Gale and Adams classification of lines, and the results are found in Table 8.

TABLE 8

Sharpness and Pressure Effect

Group	I	II	III	IV	Total
Class 1a		3	1		4
Class 3a				8	8
Class 4a			9	3	12
Class 1b	3		1	1	5
Class 2b		2			2
Class 3b				9	9
Class 4b				27	27
Class 2c	1				1
Class 4c		1		7	8
Class 5c		4		7	11
Class 5d		4	14	3	21
Class e	12	6	6		24

Gale and Adams[23] divide spectrum lines into five broad classes, according to their behavior under pressure, as follows:

1. Lines which are symmetrically reversed.
2. Lines which are unsymmetrically reversed.
3. Lines which remain bright and fairly narrow under pressure.
4. Lines which remain bright and symmetrical but become wide and diffuse under pressure.
5. Lines which remain bright and are widened very unsymmetrically toward the red.

Measures of the displacements of iron lines under pressure led Gale and Adams to form four groups of lines represented by letters a, b, c, and d. Group a includes all flame lines and these show only small displacements. Group b is a large one and includes all lines of small displacements which are not included in group a. Group c consists of lines showing much larger displacements than those of group b. Group d is made up of several scattered groups, all of which show immense displacements. If all displacement values are reduced to that of group a as the unit, the following relation exists: 1a, 1.5b, 3.4c, and 6.6d.

The table shows that lines in classes 3a, 3b, 4b, and 4c are capable of producing interference of the highest order observed, and these lines recommend themselves for use as standards. The majority of 4a and 5d lines examined reach their limiting order of interference between 40 000 and 60 000 waves.

---

[23] See note 21, p. 269.

XII. SUMMARY

Between the limits 3233A and 6750A, some 400 iron lines were either remeasured or measured for the first time by the interference method. The work was done in conformity with the recommendation of the international wave length committee. Where it was found possible, faint lines as well as strong ones were measured. Satisfactory standards were found at intervals of 10 or 15 angstroms throughout the greater part of the spectrum; there are no sharp iron lines of even moderate intensity in the region 5775A to 5934A, and the number is insufficient in the extreme red.

The spectroscope used was a 635 cm concave grating, mounted in parallel light. The greater part of the wave lengths were measured by means of three interferometers, the order of interference ranging from 20 000 to 50 000 in the case of each line. The method was that of Buisson and Fabry.

The mean difference between the present observations and the I. A. standards is about one part in four million. It is thought that some of the standards are in error by 0.002A or more.

Interferometer observations under the conditions described were found to be reasonably free from the effects of pole shifts.

Comparison with all the grating observations which have been made on the I. A. system shows, as has been found before, that more numerous secondary standards are needed in order to obtain the highest accuracy in grating work.

While grating observations often show an intensity equation, interference measurements appear to be reasonably free from this effect.

The sharpness of over 600 lines was determined and the data were correlated with data relating to pole shifts, to behavior under pressure, and to intensity. Lines showing a negative pole shift are never very sharp, while those having a positive pole shift are sometimes perfectly sharp in the center of the arc; the lines subject to a shift are more likely than are the unaffected lines to be broad, even in the center of the arc. Lines which are faint or of only moderate intensity are sharper on the average than strong lines. Still, some very strong lines are quite sharp.

The width of the average line, expressed as a proportion of the wave number, is not a function of the wave length.

WASHINGTON, December 21, 1915.

RELATION BETWEEN COMPOSITION AND DENSITY OF AQUEOUS SOLUTIONS OF COPPER SULPHATE AND SULPHURIC ACID

By H. D. Holler, Assistant Chemist, and E. L. Peffer, Laboratory Assistant

I. INTRODUCTION

In connection with an investigation on the regulation of solutions for electrodeposition, especially of acid copper sulphate solutions for electrotyping, it was found desirable to devise a simple method of determining and adjusting their composition. Since the solutions usually employed for the above purpose contain only copper sulphate and sulphuric acid, the composition of any given solution is fixed if the acid content and density at a given temperature are known. The density can be readily determined with a hydrometer, and the acidity can be ascertained with sufficient accuracy by titration with standard alkali, using methyl orange as indicator, as described by Wogrinz.[1] In order, therefore, to learn the content of copper sulphate, all that is required is a table showing the density of solutions containing known amounts of copper sulphate and of sulphuric acid.

Although the densities of solutions of copper sulphate and of sulphuric acid have been determined separately, no systematic study of the densities of solutions containing both could be found in the literature. Only in isolated cases were such data given concerning certain baths, such as those recommended by Pfanhauser,[2] Langbein-Brannt,[3] Steinach and Buchner,[4] and others.

The concentration of solutions containing both copper sulphate and sulphuric acid is limited by the fact that addition of sulphuric acid to copper sulphate solution causes a marked decrease in the solubility of the copper sulphate. Thus, while 395 grams of crystallized copper sulphate is contained in 1 liter of the saturated solution at 15° C, the addition of 100 grams per liter of sulphuric acid reduces the solubility of the copper sulphate to 215 grams per liter. Since in any practical work it is necessary to use solutions somewhat removed from the saturation point, the actual field is probably included in the range of 0 to 20 per cent of each of the constituents. Such solutions, therefore, formed the basis of this investigation. The temperature range of 25° to 40° C was selected as including the normal temperature employed in most copper plating or refining operations. Doubtless the expansion coefficients determined from such data will permit extrapolation over a moderate range above and below the temperatures used.

---

[1] Chem. Ztg., **37**, p. 869; 1913.

[2] Die Galvanoplastik, p. 37–38; 1904.

[3] Electrodeposition of Metals, 7th ed., p. 574–575, 590; 1913.

[4] Die Galvanische Metallniederschläge, p. 160–161; 1911.

II. METHOD OF INVESTIGATION

1. PREPARATION OF SOLUTIONS

In order to avoid the influence of temperature in the preparation of the solutions, they were all made of a known composition by weight, expressed in grams of each constituent per kilogram of solution. They were prepared in duplicate by mixing accurately weighed portions of water and of standardized concentrated solutions of copper sulphate and of sulphuric acid.

The stock sulphuric acid solution was prepared by diluting c. p. acid to about 12 normal with distilled water, and was standardized by the barium sulphate method with the usual precautions. It was also compared with a hydrochloric acid solution, standardized by silver chloride precipitation, through a solution of sodium hydroxide, using methyl orange as indicator.

The concentration of the sulphuric acid solution as determined by the barium sulphate method agreed with that obtained by comparison with the standard hydrochloric acid solution to within about 1 part in 1500. Weight burettes were used, the individual titrations agreeing to within less than 1 part in 2000.

The solution of copper sulphate was prepared from recrystallized salt, which gave a perfectly clear solution. The concentration of copper sulphate ($CuSO_4 \cdot 5H_2O$) was calculated from the copper content determined electrolytically, the greatest difference between any two results being 1 part in 3000. Complete removal of copper from the electrolyte was confirmed by testing with $K_4Fe(CN)_6$.

2. DENSITY DETERMINATION

Method of Determination.—The density measurements were made by the method of hydrostatic weighing, i. e., by weighing in the sample under investigation a sinker of known mass and volume. The density[5] of the liquid is then calculated by means of the equation:

$$D_t = \frac{W - \frac{(w-w_1)+(w-w_2)}{2}\left(1 - \frac{\rho}{8.4}\right)}{V_t}$$

in which

D_t = Density at temp. t
W = Mass of sinker in vacuo
w = Weighings with sinker off
w_1 and w_2 = Weighings with sinker on
ρ = Air density
8.4 = Assumed density of brass weights
V_t = Volume of sinker at temp. t

Apparatus Used.—The apparatus used is described in detail in Bureau publications (Technologic Paper No. 9 (1912) and Bureau of Standards Bulletin, Vol. 9, pp. 371–378 (1913)). A short description of the apparatus is given, as follows:

The densimeter tube (about 45 cm long and 2.5 cm in diameter) containing the sample is placed in a water bath which is kept in constant circulation. This bath is surrounded by another; also in circulation, the temperature of which is regulated by means of an electric heating coil and a brine cooling coil. The temperature of the inner bath is determined by the use of two mercury thermometers. The large sinker having a length of approximately 33 cm and diameter of 1.3 cm is attached below a small sinker and both are suspended by means of a wire from one arm of a sensitive balance. The small sinker which is in the liquid at all times serves the purpose of keeping the suspension wire taut and in position, and thus the effect of surface tension is eliminated.

Method of Making Observations.—After sufficient time has elapsed for attaining temperature equilibrium at the desired temperature, the first weighing is made with the large sinker attached, and the temperature is immediately read from each of the thermometers. Then the second weighing is made with the large sinker detached from the small sinker. In order to obviate any correction for a possible change in temperature, the first weighing is repeated and the thermometers reread. The average of the temperatures at the two weighings is taken as the true temperature. The difference between the mean of these two weighings and the second weighing is the apparent weight of the large sinker in the sample at the given temperature. After completing the observations at one point, the temperature is changed to the next and the process is repeated in the same order.

---

[5] Throughout this paper the term "density" is used to denote mass per unit volume and is here expressed in grams per milliliter. The densities are therefore numerically the same as specific gravities in terms of water at 4° C as unity.

III. RESULTS OF INVESTIGATION

The results of the density determinations and composition of the samples are shown in Table 1.

TABLE 1

Density of Copper Sulphate—Sulphuric Acid Solutions

$CuSO_4 .5H_2O$, g/kg	$CuSO_4$, g/kg	H_2SO_4, g/kg	Density,[a] 25° C	Mean density, 25° C	Density, 40° C	Mean density, 40° C	α[b]
50	31.97	0	1.03014	1.03016	1.02489	1.02488	−0.00035
50	31.97	0	1.03017		1.02488		
50	31.97	50	1.06297	1.06303	1.05637	1.05638	−.00044
50	31.97	50	1.06309		1.05639		
50	31.97	100	1.09843	1.09843	1.09060	1.09060	−.00052
50	31.97	100	1.09843		1.09060		
50	31.97	150	1.13552	1.13549	1.12669	1.12668	−.00059
50	31.97	150	1.13546		1.12667		
50	31.97	200	1.17421	1.17416	1.16453	1.16452	−.00064
50	31.97	200	1.17412		1.16452		
100	63.94	0	1.06454	1.06455	1.05871	1.05872	−.00039
100	63.94	0	1.06456		1.05874		
100	63.94	50	1.09835	1.09834	1.09097	1.09097	−.00049
100	63.94	50	1.09833		1.09097		
100	63.94	100	1.13497	1.13498	1.12642	1.12649	−.00057
100	63.94	100	1.13499		1.12656		
100	63.94	150	1.17367	1.17356	1.16417	1.16418	−.00063
100	63.94	150	1.17366		1.16420		
100	63.94	200	1.21399	1.21397	1.20379	1.20375	−.00068
100	63.94	200	1.21395		1.20371		
150	95.91	0	1.10062	1.10063	1.09428	1.09430	−.00042
150	95.91	0	1.10064		1.09431		
150	95.91	50	1.13555	1.13554	1.12765	1.12764	−.00053
150	95.91	50	1.13553		1.12764		
150	95.91	100	1.17366	1.17364	1.16457	1.16455	−.00061
150	95.91	100	1.17361		1.16453		
150	95.91	150	1.21392	1.21393	1.20391	1.20394	−.00067
150	95.91	150	1.21394		1.20396		
150	95.91	200	....	....	1.24528	1.24523	....
150	95.91	200	(c)		1.24518		
200	127.9	0	1.13833	1.13834	1.13152	1.13153	−.00045
200	127.9	0	1.13835		1.13154		
200	127.9	50	(d)	1.17485	....	1.16638	−.00056
200	127.9	50	1.17485		1.16638		
200	127.9	100	1.21449	1.21448	1.20476	1.20476	−.00065
200	127.9	100	1.21447		1.20475		
200	127.9	150	....	....	1.24579	1.24575	....
200	127.9	150	(c)		1.24571		

[a] All densities here tabulated are expressed in grams per milliliter.
[b] Change in density per degree rise in temperature.
[c] Solutions of these compositions do not exist at 25° C.
[d] Sample lost by breakage of the container.

In Table 1 the composition of the solutions is expressed in grams of $CuSO_4.5H_2O$ per kilogram of solution. The concentration in grams per liter may be readily obtained by multiplying the above concentrations in grams per kilogram by the corresponding densities. In each case density determinations were made upon duplicate solutions, and these results are seen to agree in most cases to somewhat better than 1 in the fourth decimal place. From the density data for 25° and 40° C, respectively, the thermal density coefficient α has been calculated, which may be defined as the change in density (always negative) for an increase in temperature of 1° C.

The above results are shown graphically in Fig. 1, which illustrates the effect upon the density of additions of copper sulphate to sulphuric acid solutions and of sulphuric acid to copper sulphate solutions. The curves for sulphuric acid solutions are derived from the data of Domke as given in Landolt and Börnstein, fourth edition (1912). The close agreement between the densities of solutions of the same total concentration, shown in Table 2, is illustrated in Fig. 1. The curves passing through the circles show the change in density produced by the addition of copper sulphate to solutions containing a definite amount of sulphuric acid per kilo-

TABLE 2

Showing the Relation Between Total Concentration and Density

Total concentration, g/kg	$CuSO_4$-$5H_2O$, g/kg	H_2SO_4, g/kg	Density, 25° C
50	0	50	1.0300
	50	0	1.0302
100	0	100	1.0640
	50	50	1.0630
	100	0	1.0646
150	0	150	1.0994
	50	100	1.0984
	100	50	1.0983
	150	0	1.1006
200	0	200	1.1365
	50	150	1.1355
	100	100	1.1350
	150	50	1.1355
	200	0	1.1383
250	0	250	1.1751
	50	200	1.1742
	100	150	1.1737
	150	100	1.1736
	200	50	1.1749
300	0	300	1.2150
	100	200	1.2140
	150	150	1.2139
	200	100	1.2145

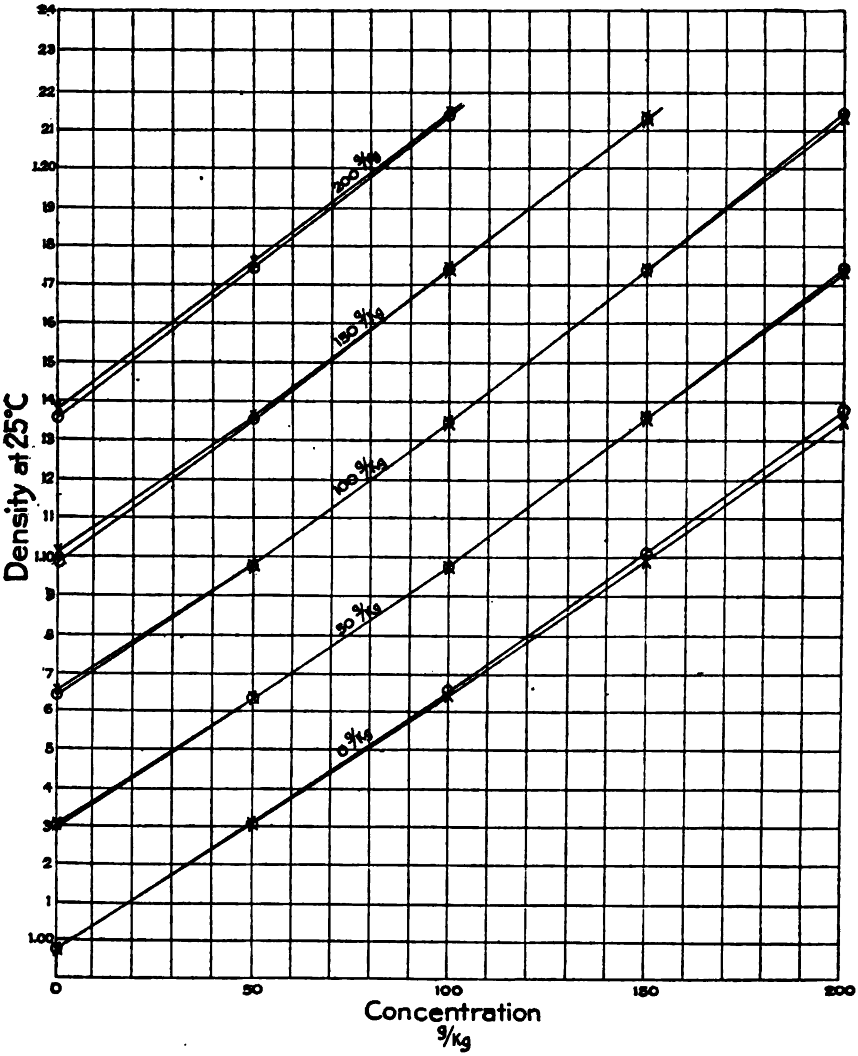


FIG. 1.—*Density of copper sulphate-sulphuric acid solutions,*
O—Sulphuric acid constant
X—Copper sulphate constant

gram of solution. Those through the crosses show the change in density produced by the addition of sulphuric acid to solutions containing a definite amount of copper sulphate per kilogram of solution, the total concentration in each case being the same as for the corresponding curve through the circles.

Example.—In the case of the curves marked 50 g/kg, the one passing through the circles shows the change in density produced by the addition of definite amounts (50, 100, 150, 200 grams) of copper sulphate to a solution containing 50 grams of sulphuric acid per kilogram of solution, and the one passing through the crosses shows the change in density produced by the addition of the same definite amounts of sulphuric acid to a solution containing 50 grams of copper sulphate per kilogram of solution.

From the above tables and curves it may be seen that—

1. Within the range studied, the density of copper sulphate-sulphuric acid solutions is approximately a linear function of the concentration.

2. The density of solutions of equal (not equivalent) concentrations of copper sulphate ($CuSO_4.5H_2O$) and of sulphuric acid is nearly identical.

3. As a natural consequence of the conclusions noted in (1) and (2), a curious relation was found to exist, i. e., that the density of solutions containing appreciable amounts of each constituent is dependent principally upon the total concentration of the two solutes, and is almost independent of their proportion. (See Table 2.) Thus, a solution containing 50 grams per kilogram of copper sulphate and 150 of sulphuric acid has practically the same density (1.1355) as has a solution containing 100 grams per kilogram of copper sulphate and 100 of sulphuric acid (1.1350). This simple relation, which is apparently only a mathematical coincidence, has been used as the basis for the curve shown in Fig. 2 in which the total concentration, in grams per liter,[6] of copper sulphate plus sulphuric acid is plotted against the density, yielding an almost straight line. The application of such a curve, or of the table derived from it (Table 3), in determining the composition of unknown solutions, is obvious, involving only a determination of the density and acidity, the latter then being deducted from the total concentration corresponding to the observed density, to obtain the copper sulphate concentration.

---

[6] Obviously, the above relation exists whether the concentration is expressed in grams per kilogram or grams per liter. The data shown in Fig. 2 and Table 3 have been calculated to grams per liter since the results of the analysis of solutions are usually expressed in that form.

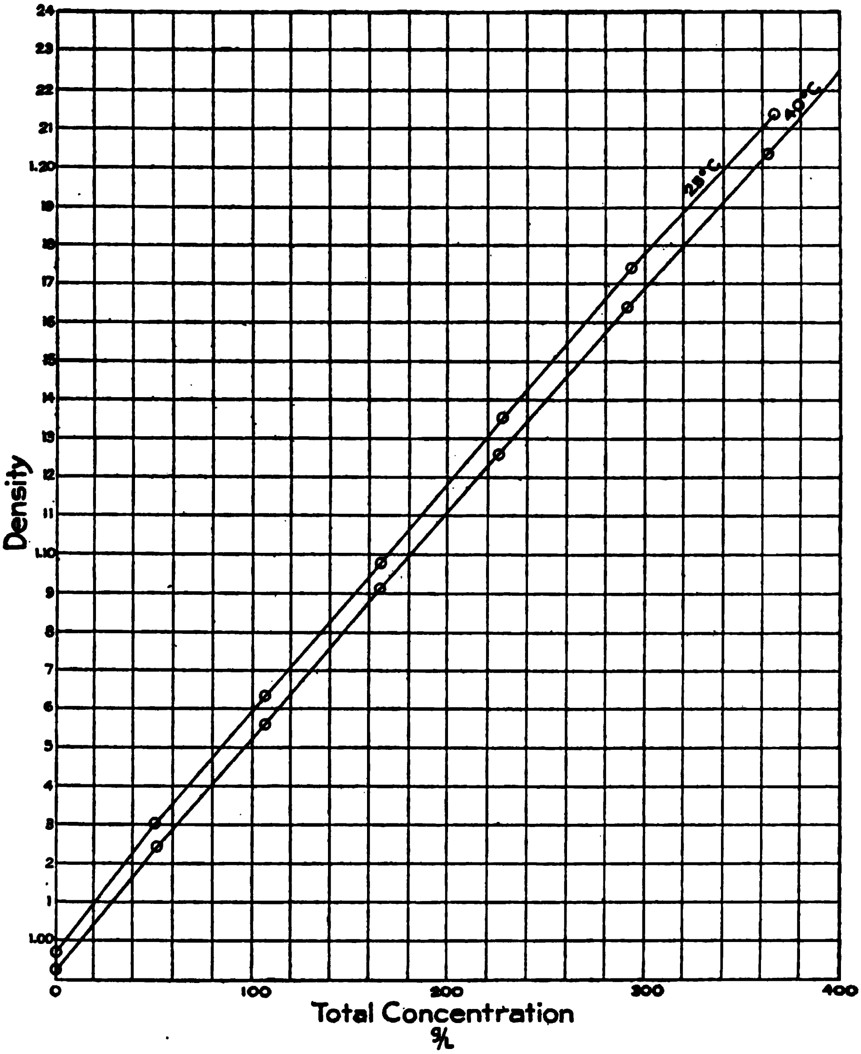


Fig. 2.—*Density of solutions of total concentration of copper sulphate plus sulphuric acid*

TABLE 3

Total Concentration of Solutions of Given Density

25° C		40° C	
Density	$CuSO_4.5H_2O+H_2SO_4$, g/l	Density	$CuSO_4.5H_2O+H_2SO_4$, g/l
1.01	20	1.01	26
1.02	36	1.02	43
1.03	52	1.03	60
1.04	68	1.04	76
1.05	84	1.05	93
1.06	100	1.06	110
1.07	117	1.07	127
1.08	133	1.08	144
1.09	150	1.09	161
1.10	166	1.10	178
1.11	183	1.11	195
1.12	200	1.12	212
1.13	217	1.13	229
1.14	234	1.14	247
1.15	251	1.15	265
1.16	268	1.16	282
1.17	286	1.17	300
1.18	303	1.18	318
1.19	321	1.19	336
1.20	339	1.20	354
1.21	357	1.21	372
1.22	375	1.22	390
1.23	393	1.23	408
		1.24	427

Details of the application of this table in the regulation of electrolytic copper baths will be given in the second edition of Bureau of Standards Circular 52.

This work was carried out under the direction of Messrs. W. Blum and H. W. Bearce.

WASHINGTON, November 27, 1915.

PROTECTED THERMOELEMENTS

By Arthur W. Gray, Assistant Physicist

Although it is customary to mount industrial thermoelements in protecting tubes provided with convenient heads for attaching the leads to the apparatus employed for measuring the electromotive force, the wires of the average thermoelement to be seen in a physical or chemical laboratory are either entirely unprotected or else merely have portions adjacent to the junctions inserted in glass or porcelain tubes. Such an arrangement may be sufficient for temporary purposes, but it is by no means the best for everyday use. Kamerlingh Onnes[1] has pointed out some of the advantages to be derived from properly protecting laboratory thermoelements, and has described in great detail the protected elements regularly used in the Leiden laboratory.[2]

Protected thermoelements have also been described by White[3] and by the present writer.[4] This paper deals with a type of mounting which has been gradually developed at the Bureau of Standards. It is applicable to elements for either high or low temperatures, and experience has shown it to be a great convenience in addition to giving adequate protection against damage by contamination or by mechanical strains.

The complete thermoelement with its ice bottle is shown in Fig. 1 just as it appears when ready for use; the three main parts are separated in Fig. 2; while a vertical section of the ice end is given by Fig. 3. The element represented is of copper and constantan. The slight modifications necessary for a platinum, platinum-rhodium element will be obvious.

---

[1] H. Kamerlingh Onnes, Leiden Communication No. 27, p. 23; 1896.

[2] H. Kamerlingh Onnes, Leiden Communication No. 27, p. 20, 1896; H. Kamerlingh Onnes and C. A. Crommelin, Leiden Communication No. 89, 1903; No. 95a, 1906.

[3] W. P. White, Journ. Am. Chem. Soc., 36, p. 2303; 1914.

[4] A. W. Gray, this Bulletin, 10, p. 464; 1914.

The silk insulation is left on the copper and the constantan wires except within the Jena combustion glass tube which covers the temperature-determining end. Within this tube the silk is removed from all but a few centimeters at the end farthest from the junction, and is replaced by a glass capillary surrounding one of the wires, because this thermoelement is used for temperatures up to over 300° C. As a precaution the silk-covered portions of the wires are treated to a bath of hot paraffin to improve the insulation. The glass protecting tube is cemented with de Khotinsky cement into a sleeve soldered to one end of a soft copper tube through which the wires pass to the head at the ice-junction end. The sleeve *A*, soldered to the ice end of this copper tube, screws into a head, *B*, of mahogany which has been prepared by keeping in paraffin at about 120° C until bubbles of steam escaping from the wood cease to be visible. This head contains the binding posts *C* and *D* for receiving the leads to the potentiometer (or galvanometer) that is used for measuring the electromotive force by which the temperature is determined. Each of these binding posts is a single piece of round copper rod with an axial hole at its upper end to receive the lead wire and an extension at its lower end for attachment to one of the wires from the thermoelement. The posts are recessed in the head to avoid danger from parasitic thermal electromotive forces.

The insulating head, *B*, screws into a short brass tube, *E*, which is provided with a knurled collar, *F*, at the top and is closed at the bottom except for a central hole through which the glass tube, *G*, extends down into the middle of the ice bath. The lower end of this tube is drawn out thin and contains the thermoelement junction, *H*. The copper wires from the ends of the constantan wire are soft soldered to the extensions of the binding posts, *C* and *D*, as indicated. In order to avoid temperature gradients across these soldered joints, very little solder is used, and, in addition, each wire, covered with its silk insulation right up to the joint, is tightly wrapped several times around the binding-post projection and then embedded in paraffin. Fused around the upper end of the tube, *G*, is a glass cup, *I*, which holds phosphorus pentoxide covered by glass wool and by the paraffin-soaked fiber washer *J*. The cup, *I*, is cemented by means of sealing wax into the brass tube *E*.

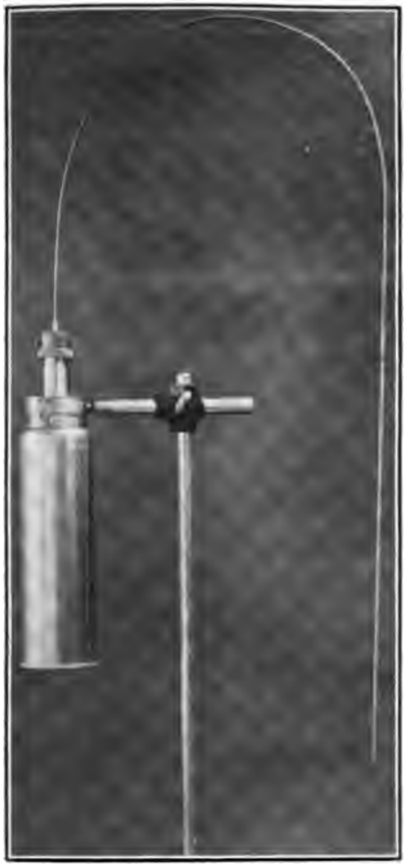


FIG. 1.—*The complete thermoelement with its ice bottle just as it appears when ready for use*

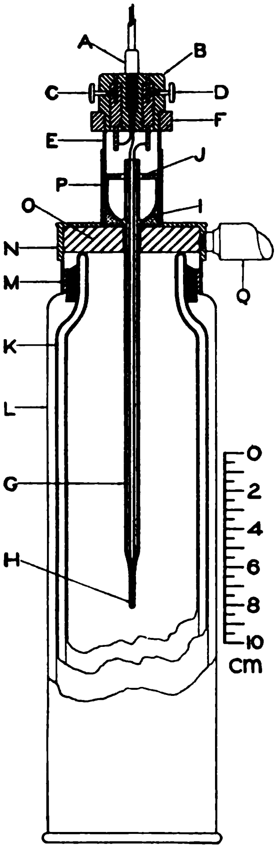


FIG. 3.—*Vertical section of the ice end*

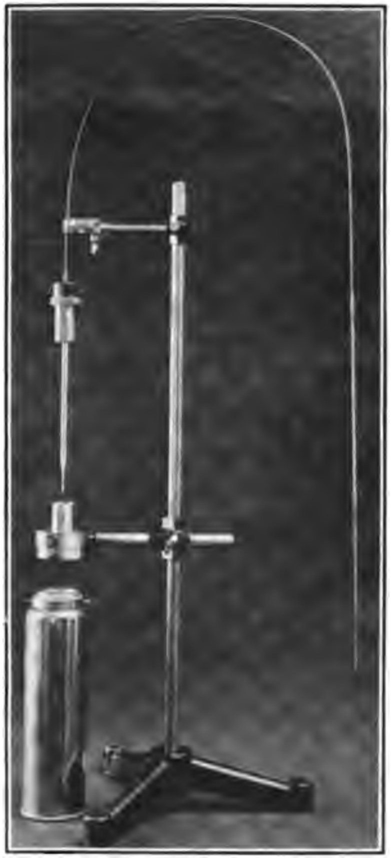


FIG. 2.—*The three main parts separated*

The ice surrounding the junction *H* is contained in a 1-quart "Caloris" vacuum jar, *K*, which comes protected by a thin nickel-plated case, *L*. Around the top of this case is soldered a stout brass ring provided with two radial projecting pins (shown in Fig. 2 but not in Fig. 3) that form part of the bayonet joint from which the ice bottle is suspended from the cap *N*. A spring (visible in Figs. 1 and 2) prevents the bayonet joint from accidentally coming loose.

Lining the cap, *N*, is the flat paraffin-soaked cork *O*, against which the vacuum jar, *K*, is pressed upward by a spiral spring in the bottom of the case *L*. Extending upward from the top of *N* is a split tube *P*, into which the tube, *E*, of the thermoelement head fits with moderate friction. The whole assemblage is supported by the rod *Q*, and is made to fit the standard laboratory clamps.

The soft copper tube uniting the two ends of the thermoelement is flexible enough to permit bending, and yet is rigid enough to retain whatever shape is given to it. The wires within are thoroughly protected from damage by sharp bending, which is liable to introduce heterogeneity. Vacuum bottles of the type described frequently retain ice in good condition for two days. When it becomes necessary to renew the ice, a slight turn of the case, *L*, frees the bayonet joint and permits lowering of the ice container without disturbing anything else.

A multiple thermoelement divided into two equal parts as advocated by White[5] can also be conveniently protected by the mounting just described if another pair of binding posts is provided.

WASHINGTON, January 27, 1916.

---

[5] W. P. White, Jour. Am. Chem. Soc., 36, p. 2305; 1914.

AN INTERLABORATORY PHOTOMETRIC COMPARISON OF GLASS SCREENS AND OF TUNGSTEN LAMPS, INVOLVING COLOR DIFFERENCES

By G. W. Middlekauff and J. F. Skogland

CONTENTS

		Page
I.	Introduction	287
II.	Laboratories cooperating	289
III.	Screens, lamps, and instructions as to methods of measurement	289
IV.	Results on the screens	291
	(*a*) Comparison of individuals' values	295
	(*b*) Comparison of laboratories' values	296
V.	Results on the lamps	297
VI.	Comparison of results on lamps and screens	300
VII.	Additional check measurements	301
VIII.	Characteristics of Bureau of Standards' observers	303
IX.	Check of former values	306
X.	Conclusion	307

I. INTRODUCTION

Since the establishment of the international candle in 1909 this unit has been maintained at the Bureau of Standards solely by means of a group of 4-wpc carbon filament incandescent lamps. With the advent of the tungsten lamp there was introduced into standardization work the difficulty of comparing lights of different colors, and at once it became desirable to have the unit well established also in tungsten lamps operated at or near their normal color.

In 1911, by common agreement between the National Physical Laboratory of England and the Bureau of Standards, each laboratory prepared a group of tungsten standards calibrated for voltage corresponding to approximately 1.5 wpc. These two groups of lamps, which were thus operated at very approximately the same color, were then exchanged and each group was remeasured by the receiving laboratory at the voltage determined by the sending laboratory. A group, similar to the one sent to England, and standardized in the same series of measurements, was retained at the Bureau, and half of the group received from England, after measurement, was returned for remeasurement.

In view of the difficulties involved in the intercomparison, the result was very satisfactory, as it showed that the two laboratories were in agreement to within the indicated precision of the measurements. In both laboratories the new standards were measured by means of Lummer-Brodhun contrast photometers of the standard type, and in terms of similar groups of 4-wpc carbon standards, the English laboratory having made the comparison by the cascade method,[1] the Bureau of Standards by the use of two calibrated blue glass screens, each of which produced a color match between the two groups of standards compared. It is obvious, therefore, that the calibration of the glass screens used by the Bureau in this intercomparison was a matter of prime importance, and for this reason a large amount of work has been done in checking, by various methods, the values first assigned.

In connection with these check measurements and after a determination of the candlepower and current of a group of tungsten substandards at several voltages had been made, and this followed by a further investigation of other groups of tungsten lamps, the voltage-current-candlepower curves were determined and accurately expressed by means of equations.[2] It was found that by employing these equations it is possible to measure tungsten lamps in color match with 4-wpc carbon standards and compute with accuracy their value at any other color within the range investigated. In this way, as well as by direct comparisons, the new tungsten standards have been rechecked a number of times by different groups of observers.

These equations have an important application also in the life testing of tungsten lamps, because in some testing laboratories it is customary to photometer the lamps at or near rated voltage and compute the voltage corresponding to the efficiency at which it is desired to burn the lamps on life test.

In the establishment of the 1.5-wpc tungsten standards and also in the determination of the characteristic equations, the photometric measurements of necessity involved color differences. Although numerous check measurements have been made and the results have been very satisfactory, it is, of course, realized that if some other group of observers had made these measurements the values obtained might have been different.

---

[1] Paterson and Dudding, Proc. Phys. Soc. London, p. 263, Apr. 15, 1915; also Phil. Mag., p. 63, July, 1915.

[2] Middlekauff and Skogland, Characteristic Equations of Tungsten Filament Lamps and their Application in Heterochromatic Photometry, Trans. I. E. S. **9**, p. 734, 1914; also this Bulletin, **11**, p. 483, 1915.

It was therefore suggested that an interlaboratory photometric comparison of lights involving color differences such as those encountered in these measurements would yield valuable information not only as to the agreement which might be reasonably expected among different groups of experienced observers, but also information as to the merits of different methods of making such measurements.

II. LABORATORIES COOPERATING

The Bureau, therefore, in May, 1914, invited several of the more important photometric laboratories of the country to cooperate with it in making measurements of this kind.

Through Dr. E. P. Hyde, Dr. C. H. Sharp, and Dr. H. E. Ives, respectively, the Nela Research Laboratory, the Electrical Testing Laboratories, and the Physical Laboratory of the United Gas Improvement Co. kindly agreed to make such measurements on glass screens and tungsten lamps as the Bureau would direct.

III. SCREENS, LAMPS, AND INSTRUCTIONS AS TO METHODS OF MEASUREMENT

For this intercomparison there were selected three blue glass screens of different color densities and marked 2B, 2½B, and 3B, respectively. 2½ B was of approximately the same color density as the screens used by the Bureau in the intercomparison with England, and was therefore such as to produce a color match between the 4-wpc carbon standards and the 1.5-wpc tungsten standards. 2B and 3B were of lesser and greater color density, respectively, than 2½B, producing a color match between the 4-wpc carbon standards and tungsten lamps at about 1.9 wpc and 1.25 wpc, respectively.

The transmission of each glass for light of 4-wpc carbon color was to be determined by each laboratory, and, in order that the proper color might be used, a carbon standard of this color at a specified voltage was sent along with the screens.

There were selected also four tungsten standards to be measured for candlepower and current at several specified voltages, the color at the lowest voltage being the same as that of the 4-wpc carbon standards. The candlepower at the other voltages was to be determined in terms of the value at the lowest voltage taken as standard, or unity.

The voltages specified for these measurements corresponded to a range from 3.1 wpc to 0.85 wpc for the tungsten lamp. The lamps were selected from those used in the investigation of the characteristic curves and included a 60-watt sintered filament lamp (No. 2608); a 60-watt "formed" drawn-wire lamp (No. 2662) with spring anchors; and two 40-watt drawn-wire lamps (Nos. 2865 and 2866).

As the purpose of the investigation was to obtain information as to methods and the agreement of different groups of observers in passing from one color to another in photometric measurements, no instructions other than those mentioned above were issued to the laboratories. It was desired that each laboratory proceed by the method it considered best, and it was not expected that a large number of measurements would be made. Hence, in view of the difficulties which were to be met in these measurements, it was hardly to be expected that values established by the Bureau as the result of a much larger number of measurements and checks would be repeated exactly. However, as will appear later, the results of all the laboratories are extremely consistent and the agreement quite satisfactory.

Two of the laboratories (E. T. L. and N. R. L.) used standard type Lummer-Brodhun contrast photometers in all the measurements. The third laboratory (U. G. I.), in the measurements on the screens, used a special flicker photometer,[3] and in the measurements on the lamps a Lummer-Brodhun photometer having in the eyepiece a cell containing a Crova solution [4] which was calibrated by a method involving the flicker photometer. All the measurements by the U. G. I. were made under selected conditions of illumination and with groups of observers selected after tests of their color vision with respect to the average of much larger groups. The data obtained are therefore valuable in making a comparison, not only of observers but also of different methods of measurement.

In no laboratory were the lamps measured at the same time as the screens, a period of from 4 to 13 months having intervened between the two series.[5] Although this was not intentional, it fortunately proved of value in showing that each laboratory consistently maintained its criterion in measurements involving a color difference. In order to avoid confusion, all the results, including those of the Bureau, on the screens are given together, as are likewise all the results on the lamps.

---

[3] H. E. Ives, Phys. Rev., p. 222; Sept., 1914.

[4] Ives and Kingsbury; Trans. I., E. S., 10, p. 716; 1915.

[5] The intercomparison was begun in June, 1914, but was not completed until in December, 1915.

IV. RESULTS ON THE SCREENS

The values for the screens are given in the four following tables, and, except as noted, they are as stated in the reports from the laboratories. The results of the three laboratories using Lummer-Brodhun photometers are grouped together, and when comparisons are made, flicker values are compared with the mean of those obtained with the Lummer-Brodhun.

TABLE 1

Values of Transmission—Bureau of Standards

Observers	2B		2½B		3B	
	Indirect method	Direct method	Indirect method	Direct method	Indirect method	Direct method
G. W. M.	0.652	0.654	0.585	0.588	0.537	0.542
J. F. S.	.651	.652	.585	.584	.538	.538
B. M.	.648	.645	.581	.575	.541	.526
H. B. S.	.652	.667	(a)	.596	(a)	.552
W. J. K.	.652	.652	.585	.580	.539	.534
W. H. V.	.651	.648	.581	.581	.535	.535
A. H. T.	.651	.655	.584	.583	.541	.535
G. J. S.	.650	.652	.585	.582	.538	.536
Mean	.651	.653	.584	.584	.538	.537

[a] Observer not available.

The photometer used was the standard Lummer-Brodhun contrast. The approximate illumination on the photometer screen was 10 meter-candles.

METHODS.—1. *Direct Method.*—The screen was placed on the test side of the photometer, the test lamp (a tungsten) was set to 4-wpc carbon color, and the comparison lamp (also a tungsten) was adjusted to match in color the light transmitted by the screen. Photometric settings were made first with the screen in place, then with it removed, there being a color difference under the latter condition. The ratio of the first settings to the second gave the transmission of the screen.

2. *Indirect Method.*—The first settings were made as in the direct method, but when the screen was removed the test lamp

was sufficiently increased in voltage to produce a color match with the comparison lamp. The ratio of the candlepower of the test lamp at these two voltages was computed by means of the voltage-candlepower equation. With this factor applied, the ratio of the settings, screen in to screen out, gave the transmission.

In both of the above methods, when the screen was removed it was replaced by a rotating sectored disk of the proper opening to make the photometer balance at about the same point as when the screen was in place.

Each value in Table 1 is the mean of about four independent determinations, the average deviation, by either method, being about 0.5 per cent.

TABLE 2

Values of Transmission—Electrical Testing Laboratories

Observers	2B			2½B			3B		
	Series 1	Series 2	Weighted mean	Series 1	Series 2	Weighted mean	Series 1	Series 2	Weighted mean
C. H. S.	0.651	....	0.651	0.583	....	0.583	0.537	....	0.537
W. F. L.	.660	0.672	.666	.594	0.586	.590	.530	0.553	.542
M. H. T.	.660	.662	.661	.585	.588	.586	.545	.546	.545
C. E. H.	.656	.652	.655	.586	.587	.586	.545	.537	.542
W. A. M.	.656	.657	.656	.587	.576	.583	.543	.539	.542
Z. N. C.	.653	....	.653	.579	....	.579	.535	....	.535
A. K.	.659	....	.659	.589	....	.589	.539	....	.539
E. H.	....	.666	.666	....	.594	.594	....	.555	.555
Mean	.656	.662	....	.586	.586	....	.539	.546	....
Weighted mean	.656	.659	.657	.585	.586	.585	.541	.543	.542

The photometer used was the standard Lummer-Brodhun contrast. The approximate illumination on the photometer screen was 2.5 to 3.8 meter-candles. As the distance between test and comparison lamps was fixed, the illumination depended upon the screen used and was highest with the screen removed.

Method: Direct.—Two carbon lamps, each operated at a voltage giving a match in color with the B. S. 4-wpc carbon lamp, were set up at opposite ends of a five-meter photometer. Settings were made, first without the screen, then with the screen interposed. This was done first on one side of the photometer and then on the other. The observers were weighted according to their experience in color difference measurements and the number of measurements made in these tests. Series 1 and 2 are independent determinations by this method. For purposes of comparison the weighted mean values (columns 4, 7, and 10) for each observer were computed by the authors.

TABLE 3

Values of Transmission—Nela Research Laboratory

Observers	2B			2½B			3B		
	Series 1	Series 2	Mean	Series 1	Series 2	Mean	Series 1	Series 2	Mean
E. P. H.	0.660	0.662	0.661	0.590	0.592	0.591	0.544	0.543	0.544
F. E. C.	.659	.661	.660	.592	.590	.591	.548	.546	.547
M. L.	.665	.660	.662	.593	.590	.592	.551	.541	.546
C. F. S.	.652	.650	.651	.578	.578	.578	.531	.530	.531
R. G. B.	.664	.662	.663	.594	.592	.593	.550	.549	.550
I. R. W.	.656	.656	.656	.584	.584	.584	.540	.538	.539
Mean	.659	.658$_5$	.659	.588$_5$	.588	.588	.544	.543	.543

The photometer used was the standard Lummer-Brodhun contrast. The approximate illumination on photometer screen was 17 meter-candles.

Method.—Same as the B. S. direct method, except that the screen and sectored disk were employed on the side of the comparison lamp, which was set to 4-wpc carbon color. Series 1 and 2 are independent determinations by this method.

TABLE 4

Values of Transmission—United Gas Improvement Co.

Observers	2B			2½B			3B		
	Series 1	Series 2	Mean	Series 1	Series 2	Mean	Series 1	Series 2	Mean
H. E. I.	0.645	0.650	0.6475	0.580	0.579	0.5795	0.534	0.527	0.5305
E. F. K.	.658	.661	.6595	.587	.588	.5875	.548	.543	.5455
F. A. S.	.645	.646	.6455	.583	.577	.5800	.528	.523	.5255
B. J.	.656	.642	.6490	.575	.574	.5745	.528	.528	.5280
D. V. L. D.	.639	.642	.6405	.585	.578	.5815	.529	.522	.5255
E. J. B.	.637	.639	.6380	.572	.573	.5725	.521	.522	.5215
W. M. W.	.640	.643	.6415	.576	.577	.5765	.521	.528	.5245
Mean	.646	.646	.646	.580	.578	.579	.530	.528	.529

The photometer used was a special flicker (see footnote 3). The brightness of the photometer field was that of a magnesium oxide surface under 25 meter-candles illumination.

Method: Direct.—The measurements were made by seven observers so selected from 25 that their mean on the color difference for which they were tested was the same as that of the 25.

TABLE 5

Deviations of Each Observer From the Mean of His Laboratory

BUREAU OF STANDARDS

Direct Method

Observers	Transmission				Deviation of observers from mean of all			Mean of deviations	Maximum difference between deviations
	2B	2½B	3B	Mean	2B	2½B	3B		
G. W. M	0.654	0.588	0.542	0.595	+0.001	+0.004	+0.005	0.003	0.004
J. F. S	.652	.584	.538	.592	− .001	.000	+ .001	.001	.002
B. M	.645	.575	.526	.582	− .008	− .009	− .011	.009	.003
H. B. S	.667	.596	.552	.605	+ .014	+ .012	+ .015	.014	.003
W. J. K	.652	.580	.534	.589	− .001	− .004	− .003	.003	.003
W. H. V	.648	.581	.535	.588	− .005	− .003	− .002	.003	.003
A. H. T	.655	.583	.535	.591	+ .002	− .001	− .002	.002	.004
G. J. S	.652	.582	.536	.590	− .001	− .002	− .001	.001	.001
Mean	.653	.584	.537	.591	.004	.004	.005	.004	.003

Indirect Method

Observers	2B	2½B	3B	Mean	2B	2½B	3B	Mean of deviations	Maximum difference between deviations
G. W. M	0.652	0.585	0.537	0.591	+0.001	+0.001	−0.001	0.001	0.002
J. F. S	.651	.585	.538	.591	.000	+ .001	.000	.000	.001
B. M	.648	.581	.541	.590	− .003	− .003	+ .003	.003	.006
H. B. S	.652	....	....	....	+ .001	....	....	....	....
W. J. K	.652	.585	.539	.592	+ .001	+ .001	+ .001	.001	.000
W. H. V	.651	.581	.535	.589	.000	− .003	− .003	.002	.003
A. H. T	.651	.584	.541	.592	.000	.000	+ .003	.001	.003
G. J. S	.650	.585	.538	.591	− .001	+ .001	.000	.001	.002
Mean	.651	.584	.538	.591	.001	.001	.002	.001	.002

ELECTRICAL TESTING LABORATORIES (Direct Method)

Observers	2B	2½B	3B	Mean	2B	2½B	3B	Mean of deviations	Maximum difference between deviations
C. H. S	0.651	0.583	0.537	0.590	−0.006	−0.002	−0.005	0.004	0.004
W. F. L	.666	.590	.542	.599	+ .009	+ .005	.000	.005	.009
M. H. T	.661	.586	.545	.597	+ .004	+ .001	+ .003	.003	.003
C. E. H	.655	.586	.542	.594	− .002	+ .001	.000	.001	.003
W. A. M	.656	.583	.542	.594	− .001	− .002	.000	.001	.002
Z. N. C	.653	.579	.535	.589	− .004	− .006	− .007	.006	.003
A. K	.659	.589	.539	.596	+ .002	+ .004	− .003	.003	.007
E. H	.666	.594	.555	.605	+ .009	+ .009	+ .013	.010	.004
Mean	.657	.585	.542	.595	.005	.004	.004	.004	.004

TABLE 5—Continued

Deviations of Each Observer From the Mean of His Laboratory—Continued

NELA RESEARCH LABORATORY (Direct Method)

Observers	Transmission				Deviation of observers from mean of all			Mean of deviations	Maximum difference between deviations
	2B	2½B	3B	Mean	2B	2½B	3B		
E. P. H	0.661	0.591	0.544	0.599	+0.002	+0.003	+0.001	0.002	0.002
F. E. C	.660	.591	.547	.599	+ .001	+ .003	+ .004	.003	.003
M. L	.662	.592	.546	.600	+ .003	+ .004	+ .003	.003	.001
C. F. S	.651	.578	.531	.587	− .008	− .010	− .012	.010	.004
R. G. B	.663	.593	.550	.602	+ .004	+ .005	+ .007	.005	.003
I. R. W	.656	.584	.539	.593	− .003	− .004	− .004	.004	.001
Mean	.659	.588	.543	.597	.003	.005	.005	.004	.002

UNITED GAS IMPROVEMENT CO. (Direct Method)

H. E. I	0.648	0.580	0.530	0.586	+0.002	+0.001	+0.001	0.001	0.001
E. F. K	.660	.588	.546	.598	+ .014	+ .009	+ .017	.013	.008
F. A. S	.646	.580	.526	.584	.000	+ .001	− .003	.001	.004
B. J	.649	.574	.528	.584	+ .003	− .005	− .001	.003	.008
D. V. L. D	.640	.582	.526	.583	− .006	+ .003	− .003	.004	.009
E. J. B	.638	.572	.521	.577	− .008	− .007	− .008	.008	.001
W. M. W	.642	.576	.524	.581	− .004	− .003	− .005	.004	.002
Mean	.646	.579	.529	.585	.005	.004	.005	.005	.005

(*a*) COMPARISON OF INDIVIDUALS' VALUES.—Another statement of the results, including only the mean of the values obtained by each observer on each of the three screens, is given in Table 5. In the fifth column is given the mean of the values of each observer for the three glasses. In the sixth, seventh, and eighth columns are the deviations of each observer's value from the mean of his laboratory on each glass. The constancy of the ratio of an observer's determination to that of his laboratory shows the consistency with which he maintains his criterion throughout the range of color included. An examination of the deviations shown in this table (excluding for the present those of the Bureau by the indirect method) shows that practically every observer, irrespective of the kind of photometer used, maintained a fairly definite relation to the mean of the observers of his laboratory. An observer's agreement with himself is indicated by the differences given in the last column of the table.

By the indirect method the variations among observers is avoided, the difficulties of measurements with a color difference having been previously met in the determination of the characteristic equation upon which, of course, the values obtained depend. As shown by the table, the deviations of all observers are about equal and about one-fourth what they are by the direct (color difference) method, although there is practically the same degree of agreement of an observer with himself. The chief advantage of this method in calibrating a screen is that a reliable result may be obtained by any group of observers, while by the direct method the results may be somewhat different, depending upon the characteristics of the observers.

(*b*) COMPARISON OF LABORATORIES' VALUES.—In order to show in the same way the agreement among the various laboratories, each taken as a unit, the final means for each laboratory are given in Table 6, in which, as before, the flicker values are compared with the mean of those obtained with the Lummer-Brodhun photometer.

TABLE 6

Deviations of Laboratories' Values from the Mean of the Three Using Lummer-Brodhun Photometers

Lummer-Brodhun Photometer

Laboratories	Transmission				Deviations from mean L-B values			Mean of deviations	Maximum difference between deviations
	2B	2½B	3B	Mean	2B	2½B	3B		
B. S.	0.653	0.584	0.537	0.591	−0.003	−0.002	−0.004	0.003	0.002
E. T. L.	.657	.585	.542	.595	+ .001	− .001	+ .001	.001	.002
N. R. L.	.659	.588	.543	.597	+ .003	+ .002	+ .002	.002	.001
Mean	.656	.586	.541	.594	.002	.002	.002	.002	.002

Flicker Photometer

U. G. I.	0.646	0.579	0.529	0.585	−0.010	−0.007	−0.012	0.010	0.005

V. RESULTS ON THE LAMPS

The results on the lamps were expressed differently by each laboratory. One (E. T. L.) gave all the values in candlepower; another (U. G. I.) reported the values as ratios using the value at the lowest voltage as unity; and the third (N. R. L.) gave the ratio of the candlepower at each voltage to the candlepower at the next lower voltage. Only one laboratory (N. R. L.) reported the values of the individual observers as was done by all in their reports on the screens. For this reason only the mean values obtained by each laboratory are given in the table of results (Table 7).

The Bureau's values of both current and candlepower were read from the characteristic curves previously determined by a group of observers whose mean was practically the same as the mean of the group that made the measurements on the screens.

In the Electrical Testing Laboratories the candlepower measurements were made by two observers (M. H. T. and C. E. H.) whose mean was the same as the mean of all the observers on the screens and the color steps were made with Wratten filters which had been calibrated by a large number of observers. In the Nela Research Laboratory the measurements on the lamps and screens were made by the same group of observers with the exception that observer M. L. made no measurements on the lamps. The cascade method was used in determining values on the lamps at the various voltages.

In the U. G. I. Laboratory the lamps were measured with a Lummer-Brodhun photometer having in the eyepiece a Crova solution calibrated on the photometric scale there used in which are involved the flicker photometer under certain chosen illumination and other conditions and the selection of observers from a large group. The group used as a basis for the Crova solution work consisted of 61 observers; the glass screen calibrations were on the basis of a group of 25

TABLE 7

Candlepower and Current Values Found by the Different Laboratories

Lamp Nos.	Volts	Relative candlepower				Amperes			
		Lummer-Brodhun photometer			Flicker photometer	B. S.	E. T. L.	N. R. L.	U. G. I.
		B. S.	E. T. L.	N. R. L.	U. G. I.				
2608	71	1.000	1.000	1.000	1.00	0.3646	0.3647	0.3646	0.3650
	81	1.674	1.677	1.684	1.68	.3944	.3944	.3944	.3951
	91	2.604	2.616	2.627	2.60	.4224	4229	.4226	.4234
	101	3.832	3.848	3.864	3.85	.4495	.4498	.4496	.4500
	111	5.392	5.434	5.460	5.34	.4753	.4758	.4756	.4757
2662	70	1.000	1.000	1.000	1.00	.3926	.3925	.3920	.3929
	80	1.687	1.695	1.696	1.69	.4245	.4249	.4244	.4253
	90	2.638	2.647	2.661	2.60	.4549	.4555	.4551	.4555
	100	3.896	3.923	3.931	3.88	.4843	.4846	.4840	.4844
	110	5.501	5.554	5.585	5.45	.5118	.5125	.5120	.5121
2865	72	1.000	1.000	1.000	1.00	.2625	.2628	.2626	.2625
	82	1.659	1.659	1.674	1.65	.2838	.2841	.2838	.2840
	92	2.567	2.579	2.615	2.56	.3037	.3041	.3036	.3035
	112	5.277	5.354	5.389	5.28	.3408	.3411	.3406	.3408
	132	9.40	9.45	9.58	9.22	.3744	.3752	.3748	.3749
2866	72	1.000	1.000	1.000	1.00	.2611	.2615	.2614	.2616
	92	2.576	2.588	2.621	2.58	.3020	.3024	.3024	.3024
	112	5.304	5.355	5.415	5.30	.3390	.3395	.3393	.3394
	122	7.191	7.223	7.321	7.16	.3562	.3568	.3566	.3566
	132	9.46	9.52	9.63	9.38	.3728	.3735	.3732	.3731

The Nela Research Laboratory gave the highest and lowest ampere values at each voltage, but to make the results uniform with the definite values reported by the other laboratories the mean of these extremes at each voltage was assumed as the correct ampere value. The deviations of the ampere values as given for the various laboratories in Table 7 from the mean of all at each voltage have been computed and found to be, on the average, about 0.05 per cent and the same for all four lamps.

In Table 8 are given the values of the ratios of the candlepower at each voltage to that at the lowest voltage, which corresponds to 4-wpc carbon color. The laboratories are arranged in the order in which they measured the lamps. As in the case of the results on the glass screens, the values obtained by each laboratory are compared with the mean of the three laboratories using Lummer-Brodhun photometers.

TABLE 8

Comparison of Candlepower Ratios Found by the Different Laboratories

Lamp Nos.	Voltage ratio	Candlepower ratio				
		Lummer-Brodhun photometer				Flicker photometer
		B. S.	E. T. L.	N. R. L.	Mean	U. G. I.
2608	81:71	1.674	1.677	1.684	1.678	1.68
2662	80:70	1.687	1.695	1.696	1.693	1.69
2865	82:72	1.659	1.659	1.674	1.664	1.65
Mean		1.673	1.677	1.685	1.678	1.673
Deviation from mean (per cent)		− .3	− .1	+ .4	.3	− .3
2608	91:71	2.604	2.616	2.627	2.616	2.60
2662	90:70	2.638	2.647	2.661	2.649	2.60
2865	92:72	2.567	2.579	2.615	2.587	2.56
2866	92:72	2.576	2.588	2.621	2.595	2.58
Mean		2.596	2.608	2.631	2.612	2.585
Deviation from mean (per cent)		− .6	− .2	+ .7	.5	−1.0
2608	101:71	3.832	3.848	3.864	3.848	3.85
2662	100:70	3.896	3.923	3.931	3.917	3.88
Mean		3.864	3.886	3.898	3.883	3.865
Deviation from mean (per cent)		− .5	+ .1	+ .4	.3	− .5
2608	111:71	5.392	5.434	5.460	5.429	5.34
2662	110:70	5.501	5.554	5.585	5.547	5.45
2865	112:72	5.277	5.354	5.389	5.340	5.28
2866	112:72	5.304	5.355	5.415	5.358	5.30
Mean		5.368	5.424	5.462	5.418	5.342
Deviation from mean (per cent)		− .9	+ .1	+ .8	.6	−1.4
2866	122:72	7.191	7.223	7.321	7.245	7.16
Deviation from mean (per cent)		− .7	− .3	+1.0	.7	−1.2
2865	132:72	9.40	9.45	9.58	9.48	9.22
2866	132:72	9.46	9.52	9.63	9.54	9.38
Mean		9.43	9.48	9.61	9.51	9.30
Deviation from mean (per cent)		− .9	− .3	+1.0	.7	−2.2

In order to determine later the agreement of the measurements on the lamps with those on the screens, percentage deviations from the mean obtained for all lamps at each voltage are given in Fig. 1, and the representative curve for each laboratory is drawn. The points at which the screens fall (i. e., the approximate voltage to which a tungsten test lamp would have to be set to obtain a color match with the screen removed) are indicated by the vertical dotted lines which intersect the curves of this figure. Correction to the mean value of the transmission of each screen may now be assigned from a consideration of the percentage difference on the lamps, as shown in the figure at the intersection with the corresponding vertical line. There is thus obtained for the screens a relation among the laboratories corresponding to that given by the curves for the lamps over the range covered by the screens.

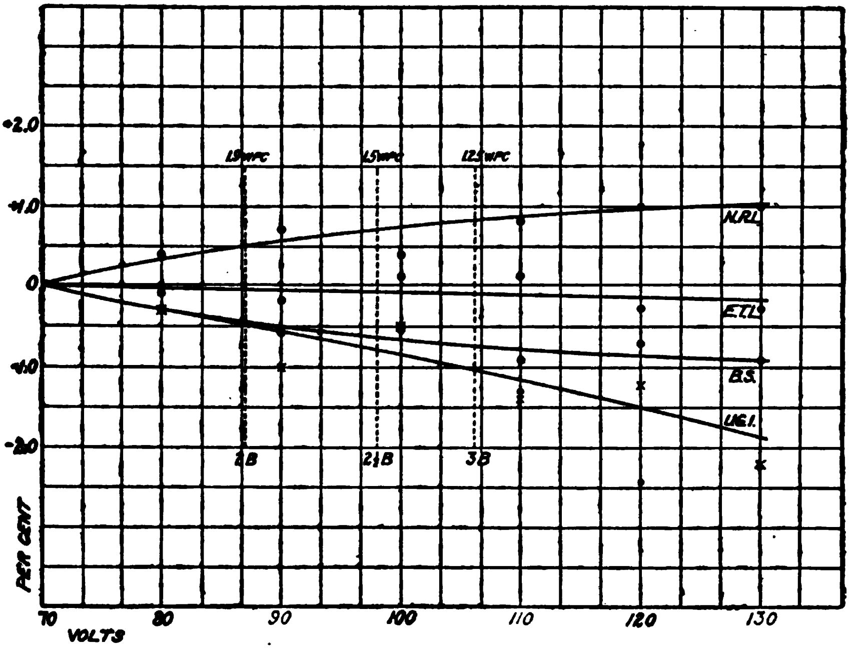


Fig. 1.—*Values on the lamps expressed as differences from the mean obtained by the three laboratories using Lummer-Brodhun photometers. The dots at 100, 110, 120, and 130 volts represent flicker values found by Crittenden and Richtmyer. (See Section VI.)*

VI. COMPARISON OF RESULTS ON LAMPS AND SCREENS

The values obtained for the glasses by direct measurement and those by computation (see Sec. V) from the results on the lamps are compared in Table 9. In the last four columns of the lower half of the table are the differences between these two sets of values. It is to be noted that for the three laboratories using the Lummer-Brodhun photometer the differences average about 0.2 per cent on the mean of the three glasses. That is, each laboratory was remarkably consistent in the two series of measurements.

TABLE 9

Comparison of Observed and Computed Values on the Screens

Screens	Values of screens as observed				
	B. S.	E. T. L.	N. R. L.	Mean	U. G. I.
2B	0.653	0.657	0.659	0.656	0.646
2½B	.584	.585	.588	.586	.579
3B	.537	.542	.543	.541	.529
Mean	.591	.595	.597	.594	.585

Screens	Relative values as computed from measurements on lamps				Differences, computed values from observed values			
	B. S.	E. T. L.	N. R. L.	U. G. I.	B. S.	E. T. L.	N. R. L.	U. G. I.
2B	0.653	0.6555	0.6595	0.6525	0.000	+0.0015	−0.0005	−0.0065
2½B	.5825	.5855	.5905	.5815	+ .0015	− .0005	− .0025	− .0025
3B	.537	.5405	.5455	.5355	.000	+ .0015	− .0025	− .0065
Mean	.591	.594	.5985	.590	.0005	.0012	.0018	.0052

In regard to the flicker values, it appears that the somewhat greater differences between the results on the glasses and the lamps is due to the values assigned to the former. As further evidence of this fact, the results by Crittenden and Richtmyer[6] on two of the lamps (Nos. 2865 and 2866), using color screens calibrated by means of a flicker photometer, agree very closely, except at 120 volts,[7] with those reported by the U. G. I., their values being indicated by dots in Fig. 1. On the other hand, the results given by the same authors for the screens by the flicker method do not agree so well with the U. G. I. values here reported.

The differences given in this table show that the first three laboratories mentioned are consistent in their measurements on the lamps and screens to within less than 0.2 per cent on the average, and that the U. G. I. computed value is practically the same as that of the Bureau of Standards.

VII. ADDITIONAL CHECK MEASUREMENTS

In order to secure a further check of the ratio of the values obtained by the Nela Research Laboratory and the Bureau of Standards, arrangements were made whereby F. E. Cady, through the courtesy of Dr. Hyde, came to the Bureau and made a number of comparative measurements with the Bureau's observers who took part in this intercomparison.

---

[6] Trans. I. E. S., **11**, p. 331, 1916.

[7] These authors state that this value should not be given equal weight with the others because only one lamp was measured at this voltage.

Comparative measurements were first made of the ratio Y/B and of the transmission of a glass screen (3G) using the flicker photometer. (See next section.) In these measurements the B. S. observers checked their former values to within the errors of observation, and hence their values in this test are not here given. Following this test, one of the lamps (No. 2661) used in establishing the voltage-candlepower curve for tungsten lamps was measured at 106 volts in terms of its value at 70 volts using a Lummer-Brodhun photometer. At the latter voltage the color of this lamp was the same as that of a 4-wpc carbon and at the upper voltage the color corresponded to that produced by glass 3B when used with a 4-wpc carbon lamp. The comparison lamp was adjusted for color match with No. 2661 at 70 volts, and the illumination on the photometer screen was adjusted to 10 meter-candles as in all the previous measurements made at the Bureau in this intercomparison. Three series of determinations of the ratio of candlepower at the two voltages were made by five observers, including Mr. Cady, and all settings were made by the contrast principle as was done in all the previous measurements at the Bureau. These results, together with the values previously obtained for 3B by these five observers (see Table 5), each in his own laboratory, are given in Table 10.

TABLE 10

Comparison of Check Measurements

Observers	Series 1	Series 2	Series 3	Mean	Transmission of 3B, from Table 5
F. E. C	4.90	4.92	4.91	4.91	0.547
G. W. M	4.85	4.87	4.81	4.85	.542
J. F. S	4.79	4.84	4.81	4.81	.538
W. J. K	4.80	4.81	4.73	4.78	.534
G. J. S	4.80	4.76	4.73	4.77	.536
Mean of the four B. S. observers	4.81	4.82	4.77	4.80	.537$_5$
Value from B. S. voltage-candlepower curve				4.81	.538

A comparison of the last two columns shows that, for the lamp, the percentage difference between the value of Mr. Cady and the mean of the B. S. observers is practically the same as for the screen, although the latter was measured under considerably different conditions of illumination in the two laboratories. As the color step was the same in each case, it can be reasonably concluded from this check that the indicated small difference between the two laboratories is real and is due, at least in a great measure, if not entirely, to a difference in the characteristics of the two groups of observers. In this connection it is of interest to note that if, in either laboratory, the first half of the observers, in the order given in Table 5, be arbitrarily taken as one group and the other half as a second group, the difference between the value by the two groups in either laboratory is comparable with the difference between the laboratories themselves.

It is obvious, therefore, that all measurements involving a color difference should be left as much as possible to the standardizing laboratory where the observers should be carefully selected, their relation to normal determined, and, if necessary, corrections made to their observations.

VIII. CHARACTERISTICS OF THE BUREAU OF STANDARDS' OBSERVERS

In the investigation by Crittenden and Richtmyer, referred to in Section VI, the observers who took part in this intercomparison determined, with the flicker photometer, a value for the ratio of the Ives-Kingsbury yellow and blue solutions,[8] and also a value for the transmission of glass screen 3G. These values, together with the values obtained with the Lummer-Brodhun photometer for glass screen 3B (Table 5, direct method), which had about the same color density as 3G, are given in Table 11. In this table are included also the mean values by the 114 observers used by Crittenden and Richtmyer, the values by Mr. Cady, and those by Dr. C. H. Sharp and Dr. H. E. Ives, who were observers in their respective laboratories and who visited the Bureau and made their measurements during the progress of the above investigation by Crittenden and Richtmyer.

---

[8] Trans. I. E. S., 10, p. 203; 1915.

TABLE 11

Data on Observers

Observers	Ratio Y+B	Transmission		Deviations from average of 114 observers		Difference between deviations
		3G. Flicker photometer	3B. Lummer-Brodhun photometer	Flicker photometer	Lummer-Brodhun photometer	
G. W. M. (B. S.)	1.025	0.540	0.542	−0.003	+0.008	+0.011
J. F. S. (B. S.)	1.103	.534	.538	− .009	+ .004	+ .013
B. M. (B. S.)	1.120	.532	.526	− .011	− .008	+ .003
H. B. S. (B. S.)	.822	.559	.552	+ .016	+ .018	+ .002
W. J. K. (B. S.)	.968	.540	.534	− .003	.000	+ .003
W. H. V. (B. S.)	.948	.548	.535	+ .005	+ .001	− .004
A. H. T. (B. S.)	1.014	.542	.535	− .001	+ .001	+ .002
G. J. S. (B. S.)	.998	.540	.536	− .003	+ .002	+ .005
Means	1.000	.542	.537	− .001	+ .003	+ .004
F. E. C. (N. R. L.)	1.044	.536	.547	− .007	+ .013	+ .020
C. H. S. (E. T. L.)	1.058	.534	.537	− .009	+ .003	+ .012
H. E. I. (U. G. I.)	.951	.542	.540	− .001	+ .006	+ .007
Average of 114 observers	.99	.543	.534	....	....	....

It is to be noted that, although there is considerable variation in the ratio Y/B among the different individuals of the Bureau's group of eight observers, the mean of all is remarkably close to the characteristic ratio (0.99) found by Crittenden and Richtmyer for the average of 114 observers. Hence, as is evident from the results on 3G, a mean value obtained by this group with a flicker photometer would require practically no correction to obtain a value corresponding to that by the average eye.

A comparison of the values on 3B shows that this group is very close to the average of the 114 observers also in its results with the Lummer-Brodhun photometer, although not quite so close as with the flicker. Whether this slightly greater variation arises from the fact that in the average eye work of Crittenden and Richtmyer the illumination was higher than in this investigation, or that in the former the photometer was used as an equality rather than as a contrast field, or (as is more likely) from the greater uncertainty of the Lummer-Brodhun photometer, is difficult to say. However, as is shown by the differences between deviations and better by means of a plot between values of Y/B and transmission (Fig. 2), all the individuals of this group do not have, with respect to the average of the 114, the same relation with the Lummer-Brodhun photometer as they do with the flicker, the first two being decidedly different by the two methods.

Now it is found that if these two observers be omitted the mean of the other six with a flicker photometer is just as close to normal as the whole group, their mean flicker values for 3G and Y/B being 0.5435 and 0.98, respectively; and, further, their mean Lummer-Brodhun value for 3B is more nearly equal to the average eye value (0.534), being 0.536 instead of 0.537, as found by the whole group. It would appear, therefore, that in order to make a comparison of former B. S. values with present (average eye) values, as is done below, there is perhaps some advantage in using the mean of this "selected" group of six.

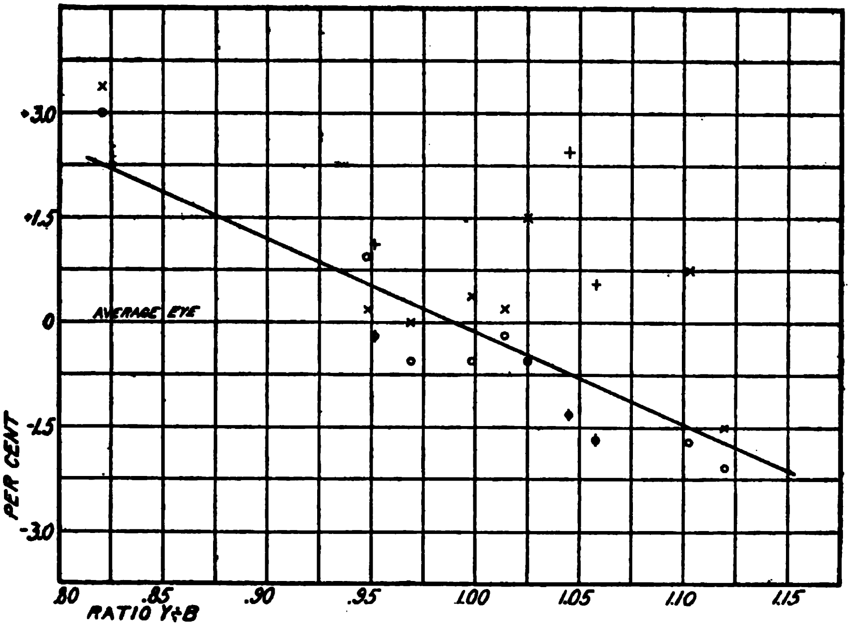


Fig. 2.—*This is a plot of the values given in Table II. The ordinates are values of transmission expressed as differences in per cent from the corresponding average value obtained by 114 observers. Lummer-Brodhun values by the eight B. S. observers are represented by X's and their flicker values by o's. The corresponding values by the three observers from the outside laboratories are represented by +'s and ɸ's, respectively. The curve represents the flicker data obtained by the 114 observers.*

Further checks on the value of 3B from the present investigation as well as from the investigation of Crittenden and Richtmyer, who determined values for 3G, which was found to be 1.6 per cent higher than 3B, are given in the following table. Nearly all of the 20 observers selected by Crittenden and Richtmyer from the 114 had considerable photometric experience, and they were well distributed with respect to the average eye characteristic as determined with a flicker photometer.

TABLE 12

Comparison of Values by Different Methods and also by Different Groups of Observers

I. With the Lummer-Brodhun photometer:	
A. As found in Crittenden and Richtmyer's investigation—	
1. By 114 observers selected at random from the Bureau of Standards scientific staff (one set each)	**3B = 0.534**
2. By 20 observers selected from the 114 (two sets each)	**3B = 0.536**
3. By 14 most consistent observers selected from the 20 (two sets each)	**3B = 0.538**
B. As found in this intercomparison—	
1. By 8 observers	**3B = 0.537**
2. By 6 observers selected from the 8	**3B = 0.536**
II. With the flicker photometer:	
A. As found in Crittenden and Richtmyer's investigation—	
1. By 114 observers (same as above)	**3B = 0.534**
2. By 20 ebservers (same as above)	**3B = 0.534**
3. By 14 observers (same as above)	**3B = 0.534**
4. By 8 observers (same as above)	**3B = 0.533**
5. By 6 observers (same as above)	**3B = 0.534**
B. As found in this intercomparison—	
1. By U. G. I., direct measurement	**3B = 0.529**
2. By computation from U. G. I. measurements on lamps with the Lummer-Brodhun photometer and a Crova solution calibrated by a method involving the flicker photometer	**3B = 0.536**

From the above comparison it is apparent that for the color difference here represented the group of eight, as well as the group of six, is as nearly normal as it is possible for a small group to reproduce average eye values with the respective photometers mentioned.

IX. CHECK OF FORMER VALUES

Screen 2½B was chosen for this intercomparison because it had approximately the same color value as the glasses used in the intercomparison with the National Physical Laboratory. The mean values found for this screen by the group of eight and by the group of six were 0.5836 and 0.5828, respectively. The relative value of 2½B to 3½C, which is one of the glasses used in the B. S.-N. P. L. intercomparison, has been recently determined and found to be as follows:

$3\frac{1}{2}C = 2\frac{1}{2}B + 0.010$

Therefore, by the group of 8 observers.................. $3\frac{1}{2}C = 0.5836 + 0.010 = 0.5936$

And by the group of 6 observers...................... $3\frac{1}{2}C = 0.5828 + 0.010 = 0.5928$

Value used in the B. S.-N. P. L. intercomparison in 1911.................... 0.5924

Although in the earlier measurements made by the Bureau of Standards no method of selection of observers was employed and the illumination used was that employed in other work done at the Bureau and was much lower than that used in the recent investigation of Crittenden and Richtmyer, nevertheless it appears from the agreement in the above values that the considerable deviations from the mean of some of the observers at that time were such that the plus and minus deviations substantially counterbalanced each other, and the figures then obtained by the Bureau with the Lummer-Brodhun photometer correspond closely to those now obtained by an average eye working under the higher illumination used by the investigators mentioned. Of course, it would not be expected that such deviations would all be in one direction, but that they were averaged out so completely was a matter of good fortune.

X. CONCLUSION

The results of this intercomparison show quite conclusively that in each laboratory, regardless of the kind of photometer used, even though a considerable color difference was involved, each observer maintained a fairly constant criterion with respect to the mean. The same is true of each laboratory in respect to its relation to the mean of all, as judged by the measurements on the glass screens and those made on the lamps some months afterward.

Considering the difficulties involved in the measurements, the different characteristics of observers and the wide difference in illumination employed, covering probably a range of ten times, the agreement among the laboratories must be considered remarkably good. It is true, however, that although the differences are small they are not negligible in precision photometry.

It is evident, therefore, that measurements to establish standards involving a color difference should be left as much as possible to the standardizing laboratory where the observers must be carefully selected and a considerable number employed and the kinds of instruments and the conditions of illumination, etc., definitely fixed.

An examination of the Bureau's observers who took part in this work shows that their mean characteristic is very approximately the same as that of the "average eye," as determined from a test of 114 observers taken at random from the Bureau's scientific staff.

Further evidence is obtained as to the accuracy of the values assigned to a group of 1.5-wpc tungsten standards used in a previous intercomparison with the National Physical Laboratory of England.

The authors express the Bureau's appreciation of the cooperation of the laboratories, and of those who represented them, in carrying out this investigation.

WASHINGTON, January 22, 1916.

AN INVESTIGATION OF THE LAWS OF PLASTIC FLOW

By Eugene C. Bingham

CONTENTS

		Page
I.	Introduction	309
II.	Experimental	311
	1. Description of apparatus	311
	2. Experimental results	312
III.	Types of viscous and plastic flow	319
	Case 1. Viscous flow—Homogeneous fluids	319
	Case 2. Viscosities additive—Emulsions	320
	Case 3. Fluid mixtures—Fluidities additive	321
	Case 4. Suspensions—The simplest case	326
	Case 5. Seepage	326
	Case 6. Nonplastic suspensions	327
	Case 7. Plastic suspensions	329
IV.	Discussion of experimental data	331
	1. Law of pressures	331
	2. Friction constant	335
	3. Mobility	336
	4. Slipping	340
V.	Relation of results to earlier work on plasticity	341
VI.	Models of plastic flow	351
VII.	Summary	352

I. INTRODUCTION

Plastic flow is of importance in many diverse fields, such as geophysics, colloidal chemistry, metallurgy, ceramics, road building, and the lime and cement business. The property of plasticity, like ductility and malleability, is not at present strictly definable, although the term is much more familiar than the strictly defined terms "viscosity" and "fluidity."

In the study of plastic flow it has already been shown that most homogeneous solids will flow somewhat after the manner of liquids, if subjected to sufficient pressure. Copper, steel, lead, ice, menthol, glass, and asphalt fall in this class in so far as they may be regarded as homogeneous solids. But ordinarily plastic substances are not homogeneous solids but suspensions of finely divided solids in fluids, such as paint in oil, lime in water, and especially clay in water. Numerous papers have been devoted to the explanation of this latter type of plasticity.

Since glass and other similar bodies are often regarded not as solids but as very viscous liquids, the demarcation of viscous flow from plastic flow has not been sharply made. In fact, attempts have been made to give numerical values to the viscosity of ice, menthol, glass, and pitch, and Tammann[1] defines plasticity in a perfectly definite manner as the reciprocal of viscosity—in other words, plasticity and fluidity are synonymous.

Unfortunately, for the sake of simplicity, this definition is clearly untenable. If any finely divided solid, such as clay, be suspended in a liquid, the fluidity is lowered rapidly and in a perfectly linear manner, so that at a comparatively low concentration of clay the fluidity, as measured in the ordinary viscometer, approaches zero. Thus Durham and Bingham[2] found that a certain clay suspended in water gave a zero fluidity when the volume percentage had reached 6.95 (14.6 per cent by weight), this being independent of the temperature. This concentration apparently serves to sharply demarcate plastic from viscous flow. Suspensions more dilute than this critical concentration are subject to viscous flow, while those containing more solid in suspension are plastic.

These results are in harmony with the views of Maxwell,[3] which are so important that we quote them at length:

> If the form of the body is found to be permanently altered when the stress exceeds a *certain* value, the body is said to be soft or plastic and the state of the body when the alteration is just going to take place is called the limit of perfect elasticity. If the stress, when it is maintained constant, causes a strain or displacement in the body which increases continually with the time, the substance is said to be viscous. When this continuous alteration of form is only produced by stresses exceeding a certain value, the substance is called a solid, however soft it may be. When the very smallest stress, if continued long enough, will cause a constantly increasing change of form, the body must be regarded as a viscous fluid, however hard it may be.
>
> Thus a tallow candle is much softer than a stick of sealing wax; but if the candle and the stick of sealing wax are laid horizontally between two supports, the sealing wax will in a few weeks in summer bend with its own weight, while the candle remains straight. The candle is therefore a soft (or plastic) solid, and the sealing wax a very viscous fluid.
>
> What is required to alter the form of a soft solid is sufficient force, and this, when applied, produces its effect at once. In the case of a viscous fluid it is time which is required, and if enough time is given the very smallest force will produce a sensible effect, such as would be produced by a very large force if suddenly applied.
>
> Thus a block of pitch may be so hard that you can not make a dint in it with your knuckles; and yet it will, in the course of time, flatten itself out by its own weight and glide down hill like a stream of water.

The italics and parenthesis are ours.

The experiments of Bingham and Durham[2] support the definition by Maxwell that a plastic body is one in which the form of the body is found to be permanently altered when the stress exceeds a certain value. These experiments indicate that the demarcation between the two régimes is very sharp, but they do not give any clue in regard to the laws of plastic flow, which must be known before a rational basis can be obtained for the quantitative measurement of plasticity.

---

[1] Ann. der Phys., 7, p. 198; 1902.

[2] Am. Chem. Jour., 46, p. 278; 1911.

[3] Theory of Heat.

II. EXPERIMENTAL

1. DESCRIPTION OF APPARATUS

The essential part of the apparatus used for the study of plastic flow is shown in Fig. 1. Pressure is admitted at *F* from an air reservoir connected with a water manometer. The chamber *D*, 2 cm in diameter and 4.4 cm deep, contains the plastic substance to be forced through the glass capillary *A*, cemented into the brass cap *B*, this last being screwed tightly into the main part, using a lead gasket. The receiver *K* is held in place by a rubber collar *C* during the flow, but after the efflux the apparatus is removed from the constant-temperature bath in which it is immersed, the receiver closed with a rubber stopper, and weighed. At *M* there is a connection for rubber tubing leading out of the bath in order to keep the space in the receiver at atmospheric pressure.

On exposure to ordinary air the materials used were liable to changes in concentration due to evaporation, hence it was necessary to work in an atmosphere saturated with water vapor, using a chamber whose walls were kept moistened. The material was made up by weight in a glass-stoppered weighing bottle and then thoroughly shaken until the mass was uniform. Experiments were made to determine whether any change in the rate of flow would result from allowing the material to stand for several hours after being prepared, but no change was observed.

The possibility of the material changing its concentration on account of settling could only be counteracted by shaking the material in the apparatus immediately before a determination; but with materials which settle out rapidly, even

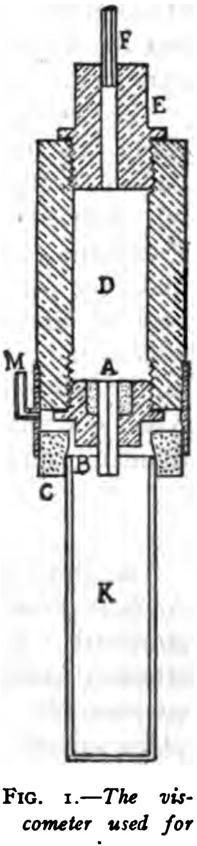


FIG. 1.—*The viscometer used for very viscous or plastic materials*

with this precaution, a difficulty arises from the solid material which packs into the mouth of the capillary. This difficulty was obviated by allowing a small amount of material to flow through the capillary into an extra receiver just before attaching the weighed receiver.

Since plastic materials take the temperature of the bath slowly, on account of the absence of convection currents, a considerable time was allowed for the equilibrium to be reached. Most of the experiments were carried out at 25° C, which was as near as practicable to the room temperature.

To determine whether there was noticeable separation of the components in the process of flow the material which had passed through the capillary was evaporated to dryness and weighed, but the separation was only noticeable when the rate of flow was very small (cf. Table 15).

The principal material used for this investigation was English china clay from St. Austell, Cornwall, England. Nearly all of it passed through a 200-mesh sieve. It was then put through the air analyzer devised by Pearson and Sligh, of the Bureau of Standards (Technologic Paper No. 48), using a 0.001-inch nozzle and 45 g per square centimeter air pressure. As a result 92 per cent of the material was obtained as an impalpable powder, which under the microscope seemed to consist of particles, of fairly uniform size, being rounded in shape and, very roughly, 0.002 mm diameter. Perhaps 1 per cent of the particles had a diameter ranging as high as 0.005 mm.

2. EXPERIMENTAL RESULTS

The dimensions of the six capillaries used are given in Table 1. A Zeiss standard millimeter was calibrated against a known standard belonging to the Bureau of Standards. The Zeiss standard millimeter was used to calibrate the Zeiss micrometer eyepiece No. 723. The ends of the capillaries were ground to a plane surface so that it was easy to obtain a good setting. The values given are in all cases the average of several readings. From these values the average radius, given in the next to the last column, was calculated by the known formulas.

TABLE 1

Dimensions of Capillaries Used

No.	The values of the radius in centimeters at the two ends (L and R) in the major and minor axes					
	L major	L minor	R major	R minor	Average radius[a] in centimeter at 20°	Length in centimeters at 20°
1	0.02974	0.02736	0.02965	0.02736	0.02848	2.468
2	.02977	.02714	.02974	.02707	.02846	1.2195
3	.02953	.02701	.02949	.02721	.02826	4.412
6.1	.06054	.05574	.05954	.05590	.05785	5.011
6.2	.06020	.05609	.06057	.05593	.05811	2.509
6.3	.06175	.05631	.06090	.05563	.05850	9.998

[a] Average radius calculated according to formula, cf. Zeitschr. *f.* physik. Chem., 80 p. 683; 1912.

In the following tables all of the measurements obtained are given, numbered in chronological order, but arranged here in the order of increasing pressure. In the second column is given the time, t, of outflow in seconds, in the third column the pressure, *P*, in grams per square centimeter, corrected, except for kinetic energy and the hydrostatic head within the instrument. The kinetic energy correction is given in the seventh column. Experiments were made to determine the value of the hydrostatic head by varying the amount of material within the instrument when the flow began. For since the materials used have infinite viscosity as ordinarily measured and because in the course of the flow the material does not preserve anything like a horizontal surface, it is not evident a priori what the correction in question should be; in fact, whether it should be positive or negative. Experiment, however, failed to give any clear indication, hence it seemed best to neglect this correction altogether for the present. This correction could have been made small by using only relatively large pressures, but in this preliminary research it seemed best to use a wide range of pressures in order to discover disturbing conditions and thereby the best conditions for future work.

The densities of the suspensions, ρ, were calculated from the density of water and the density of the clay, which was determined to be 2.613 at 25° C. To obtain this density a 50 ml flask was filled with clay and weighed. Carbon tetrachloride was added, heated to boiling until the air was expelled, cooled to 25° C, and weighed.

TABLE 2

Experiments with Capillary No. 1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec. $\times 10^8$	C(P–f)t $\times 10^8$	$C'\rho/t \times 10^8$	μ[a]
13	600.2	80.1	2.119	2.45	88	0	11.42
18	300.0	101.4	1.938	4.47	537	0	1.86
14	300.2	101.8	2.166	5.00	489	0	2.04
15	300.3	102.3	2.126	4.91	509	0	1.97
16	360.0	102.9	2.307	4.21	607	0	1.65
17	126.0	103.3	0.818	4.50	578	0	1.73
....	....	....	....	....	....	....	....
20	300.1	126.8	2.395	5.53	905	0	1.10
19	300.2	128.6	2.660	6.14	846	0	1.18
2	180.0	154.6	2.353	9.05	868	0	1.15
1	180.1	156.5	2.326	8.95	900	0	1.11
7	200.0	178.1	3.412	11.82	864	0	1.16
[3	180.0	191.0	2.383	9.17	1264	0	0.79]
8	180.3	206.1	3.738	14.37	915	0	1.09
9	192.3	206.8	4.299	15.49	853	0	1.17
11	180.2	234.7	5.194	19.97	805	0	1.24
10	108.7	235.2	2.770	17.66	576	0	1.74
4	180.1	270.9	6.040	23.23	852	1	1.18
....	....	....	....	....	....	....	....
5	102.0	288.0	3.228	43.84	491	1	2.04
12	99.6	294.3	6.029	41.94	529	1	1.89
6	103.2	295.3	6.684	44.87	497	1	2.02

Average mobility for medium pressures, 1.17.

Average mobility deviation from mean, 0.04.

[a] The definition of the "mobility," which we represent by μ, will appear later, cf. p. 336 et seq. The significance of the constants C and C' are also given on p. 336. The friction constant f is discussed on pp. 331 and 335.

TABLE 3

Experiments with Capillary No. 2, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume ($\rho=1.443$, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec. $\times 10^8$	C(P–f)t $\times 10^8$	$C'\rho/t \times 10^8$	μ
29	2100.2	40.9	1.056	0.3	....	....	....
36	780.0	41.8	3.055	2.71	....	....	....
28	600.2	50.6	2.126	2.45	....	....	....
27	399.0	70.0	2.410	4.18	....	....	....
24	300.3	79.9	2.129	4.91	80	....	....
25	200.0	84.7	1.837	6.36	217	....	....
....	....	....	....	....	....	....	....
23	280.0	90.7	2.943	7.21	364	0	2.75
26	231.4	91.8	2.442	7.31	390	0	2.57
22	240.2	99.9	3.786	10.92	415	0	2.41
21	190.0	107.0	4.474	16.32	368	1	2.72
30	180.1	108.6	3.794	14.60	423	1	2.37
31	180.2	118.1	4.200	16.15	514	1	1.95
33	98.3	127.4	3.406	24.00	426	1	2.35
32	90.0	140.4	4.154	31.98	404	2	2.49
34	88.3	150.8	5.012	39.32	383	2	2.62
35	90.0	157.8	5.426	41.77	386	2	2.60

Average mobility for medium pressures, 2.48.

Average mobility deviation from mean, 0.17.

TABLE 4

Experiments with Capillary No. 3, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume (ρ=1.443, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec.×10^3	C(P-f)t ×10^8	C′ρ/t×10^8	μ
46	720.0	105.4	3.094	2.98	511	0	1.96
45	360.2	135.7	2.246	4.32	743	0	1.34
38	360.0	158.6	1.994	3.84	1168	0	.88
41	865.2	190.2	7.570	6.06	1020	0	.98
42	398.3	234.7	3.858	6.71	1298	0	.77
43	300.0	236.4	4.168	9.62	916	0	1.09
44	200.0	241.3	3.281	11.36	800	0	1.25
39	300.0	280.9	4.739	10.94	1031	0	.97
40	330.0	297.7	4.938	10.37	1178	0	.85

Average mobility for medium pressures, 1.02.
Average mobility deviation from mean, 0.16.

TABLE 5

Experiments with Capillary No. 6.1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume (ρ=1.443, Using Pure Water; Friction Constant=78)

No.	t	P	Wt.	Vol. per sec.×10^3	C(P–f)t ×10^8	C′ρ/t×10^8	μ
60	180.2	99.6	4.764	18.32	1012	0	0.99
61	180.3	100.3	4.698	18.05	1088	0	.92
47	180.1	119.5	5.566	21.41	1668	0	.60
53	90.0	149.2	5.502	42.36	1445	0	.69
54	120.2	150.6	7.180	41.38	1508	0	.66
48	129.6	154.4	5.192	27.76	2369	0	.42
51	77.4	171.6	9.038	80.85	996	1	1.00
52	87.6	172.3	9.943	78.67	1028	1	.97
58	80.4	174.6	7.826	67.44	1232	1	.81
57	165.0	175.0	8.591	36.07	2308	1	.43
56	156.5	194.7	15.473	68.56	1463	1	.68
55	106.5	199.3	13.896	90.34	1154	1	.87
50	88.0	208.4	8.772	69.07	1587	1	.63
49	20.0	211.3	2.383	82.52	1389	1	.72
[59	48.0	236.0	15.258	220.2	617	3	1.63]
62	114.6	260.9	14.41	87.09	1807	1	.55

Average mobility, 0.73.
Average mobility deviation from mean, 0.16.

Bingham and Durham have found that acids and alkalies have very great effect upon the rate of flow of suspensions. To determine whether or not alkalies from the glass or carbonic acid from the air affects the constancy of these determinations, suspensions were made up in a one-tenth per cent solution of potassium carbonate.

TABLE 6

Experiments with Capillary No. 6.1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume (ρ=1.443, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec.$\times 10^8$	C(P-f)t $\times 10^8$	$C'\rho/t \times 10^8$	μ
67	299.7	49.9	9.59	22.18	....	....	....
66	206.5	60.0	11.50	38.57	....	....	....
....	....	....	....	....	....	....	....
68	105.3	79.7	11.55	76.01	229	1	4.39
65	57.4	101.4	14.41	173.9	261	2	3.87
69	36.0	124.0	12.69	244.3	227	3	4.47
64	33.8	148.1	19.49	399.5	191	5	5.42
70	27.4	158.6	15.17	383.5	222	5	4.60
63	22.7	200.0	18.37	560.7	215	7	4.82

Average mobility for medium pressures, 4.60.
Average mobility deviation from mean, 0.35.

The mobility is much greater with a trace of alkali present. The effect is very marked even when shaking the material up with the solution, being evidently "thinner."

TABLE 7

Experiments with Capillary No. 6.3, at 25° C, with 50 Per Cent Clay by Weight or 27.6 Per Cent by Volume (ρ=1.443, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec.$\times 10^8$	C(P-f)t $\times 10^8$	$C'\rho/t \times 10^8$	μ
83	270.9	88.8	16.28	41.5	253	0	3.96
71	120.2	117.4	13.45	77.5	337	1	2.98
72	88.9	147.6	14.20	110.8	358	1	2.80
79	78.2	163.8	15.91	141.0	334	1	3.01
76	60.6	175.3	14.87	170.0	307	1	3.27
81	48.7	185.7	16.74	238.2	239	1	4.21
75	51.2	195.6	15.23	206.1	298	1	3.37
....	....	....	....	....	....	....	....
74	44.9	197.1	17.26	266.3	233	2	4.32
73	41.0	198.2	16.76	283.2	221	2	4.57
80	37.3	211.7	16.34	303.5	226	2	4.46
77	32.8	238.7	16.06	339.5	238	2	4.24
78	23.3	262.1	15.77	468.8	195	3	5.21
82	22.4	264.4	13.88	429.2	215	3	4.71

Average mobility for medium pressures, 3.37.
Average mobility deviation from mean, 0.41.

These values are irregular, but particularly at the higher pressures.

TABLE 8

Experiments with Capillary No. 6.2, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume (ρ=1.443, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec.×10^8	C(P–f)t ×10^8	C′ρ/t×10^8	μ
88	190.7	33.5	12.10	...	...	...	...
87	73.5	50.4	17.54	...	...	...	...
86	55.9	59.9	14.20	...	...	...	...
85	30.4	68.5	10.63	242	63	6	17.7
...	...	...	...	...	...	...	...
84	24.8	80.2	10.32	288	125	7	8.47
89	16.8	117.0	14.20	585	172	15	6.38

Average mobility for medium pressures, 7.42.

Average mobility deviation from mean, 1.04.

TABLE 9

Experiments with Capillary No. 6.2, at 25° C, with 60 Per Cent Clay by Weight or 36.40 Per Cent by Volume (ρ=1.585, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=119)

No.	t	P	Wt.	Vol. per sec.×10^8	C(P–f)t ×10^8	C′ρ/t×10^8	μ
100	180.2	118.3	3.378	11.8	...	...	...
96	400.0	136.8	5.245	8.3	...	...	...
...	...	...	...	...	...	...	...
94	299.7	155.3	4.223	8.9	7131	0	0.140
95	245.1	174.1	4.993	12.8	7495	0	.133
93	180.2	200.2	4.848	17.0	8368	0	.120
92	182.1	234.5	7.128	24.7	8184	1	.122
91	209.8	263.8	10.03	30.2	8398	1	.119
98	180.2	268.8	9.236	32.3	8101	1	.124
97	190.1	296.3	8.271	27.45	11298	1	.088
99	132.6	298.4	7.374	35.1	8945	1	.112

Average mobility for medium pressures, 0.119.

Average mobility deviation from mean, 0.10.

TABLE 10

Experiments with Capillary No. 6.2, at 25° C, with 70 Per Cent Clay by Weight or 47.10 Per Cent by Volume (ρ=1.758, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=?)

No.	t	P	Wt.
102	2730	272.6	0.794
101	670	302.0	.738

The viscosity of a suspension consisting of 25 per cent clay by weight or 11.28 per cent by volume, ρ = 1.179, using 0.1 per cent of potassium carbonate was determined in a horizontal tube viscometer to be 0.0190, at 25° C, which corresponds to a fluidity of 52.7.

TABLE 11

Experiment with Capillary No. 1, at 25° C, with 47 Per Cent Clay by Weight or 25.28 Per Cent by Volume (ρ=1.405, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=40)

No.	t	P	Wt.	Vol. per sec.$\times 10^3$	C(P-f)t $\times 10^3$	$C'\rho/t \times 10^3$	μ
112	229.8	43.3	5.114	....	....	....	....
111	200.0	57.7	3.682	13.1	138	0	7.24
110	179.8	70.3	6.052	23.9	130	1	7.73
113	150.0	94.1	8.321	39.5	141	1	7.11
105	139.8	95.2	9.144	46.5	122	1	8.30
106	73.9	142.4	7.883	75.9	138	2	7.33
107	86.0	199.5	14.80	122.0	134	3	7.64
109	59.8	230.1	13.74	163.5	119	4	6.12
108	63.6	248.0	17.26	193.1	111	5	9.48

Average mobility for medium pressures, 7.35.

Average mobility deviation from mean, 0.46.

TABLE 12

Experiments with Capillary No. 1, at 40° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume (ρ=1.438, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec.$\times 10^3$	C(P-f)t $\times 10^3$	$C'\rho/t \times 10^3$	μ
114	240.0	106.8	11.69	33.8	143	2	7.08
115	119.4	148.0	12.78	75.6	122	5	8.54
116	112.2	202.1	15.73	97.4	150	6	6.95
119	102.5	207.9	15.40	104.4	146	7	7.19
117	66.0	247.8	14.94	157.3	123	10	8.89
118	50.1	280.4	12.81	177.8	128	12	8.63

Average mobility, 7.88.

Average mobility deviation from mean, 0.81.

TABLE 13

Experiments with Capillary No. 1, at 25° C, with 50 Per Cent Clay by Weight or 27.62 Per Cent by Volume (ρ=1.443, Using 0.1 Per Cent Solution of Potassium Carbonate; Friction Constant=59.5)

No.	t	P	Wt.	Vol. per sec.$\times 10^3$	C(P-f)t $\times 10^3$	$C'\rho/t \times 10^3$	μ
125	309.7	89.62	9.932	22.2	139	1	7.22
124	259.4	127.6	13.75	36.7	190	1	5.28
120	241.6	156.0	17.27	49.8	199	1	5.06
126	171.2	170.9	14.13	57.2	200	2	5.04
127	147.8	188.5	14.20	66.6	199	2	5.07
121	132.3	202.3	16.62	87.0	168	2	6.02
123	84.8	249.0	14.22	116.1	167	3	6.08
122	78.6	287.2	14.84	130.8	168	3	6.05

Average mobility for medium pressures, 5.11.

Average mobility deviation from mean, 0.08.

III. TYPES OF VISCOUS AND PLASTIC FLOW

CASE 1. VISCOUS FLOW—HOMOGENEOUS FLUIDS.—If two horizontal planes at unit distance apart are acted upon in opposite directions by a unit tangential force per unit area, the velocity of one plane in respect to the other is a measure of the fluidity of the substance filling the space between the planes. Viscosity (η) is the reciprocal of the fluidity (φ). In general, if dr is the distance between two planes acted upon by the tangential force P, the displacement produced per unit of time is

$$dv = \varphi P dr \qquad \text{(1)}$$

In order to deduce a formula which will permit of the experimental determination of viscosity, several assumptions must be made; they are as follows:

1. It is generally assumed that where two substances, or two phases of the same substance, come in contact, the velocity of both is identical at their surface of separation, i. e., there is no "slipping."

2. Each stratum of the fluid must move solely in the direction of the shearing force, i. e., there must be *stream line motion* only. Otherwise a correction must be made for the kinetic energy improperly lost.

3. It is assumed that the resistance to flow varies directly as the rate of shear, and becomes zero when the shear is zero.

4. It is further assumed that the resistance is directly proportional to the area of surface, but independent of the curvature of the surface.

With these assumptions the viscosity formula for a straight capillary tube, squarely cut off at the ends and having a bore which is a true circular cylinder, is

$$\eta = \frac{\pi g r^4 P t}{8V(l+\lambda)} - \frac{m\rho V}{8\pi t(l+\lambda)} \qquad \text{(1a)}$$

where V is the volume of flow in cubic centimeters, l the length, and r the radius of the capillary in centimeters, t the time in seconds, P the average difference in pressure in grams per square centimeter at the two ends of the capillary, g is the gravity constant, m is a constant equal to 1.12 according to Boussinesq,[4] λ is a correction to be made to the length of the capillary because of the stream line motion not becoming established at the entrance and is negligible when the length of the capillary is many times the diameter. This formula gives the viscosity (η) in c. g. s. units.

---

[4] Compt. rend., **110**, pp. 1160, 1238 (1890); **113**, pp. 9, 49 (1891).

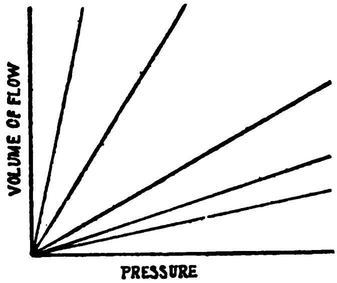


FIG. 2.—*Typical diagram of viscous flow. This is in marked contrast with the diagrams of plastic flow, Figs. 8 and 9.*

It is thus a fundamental characteristic of viscous flow that, so long as the pressure is small, the volume of the flow varies directly as the pressure. Or expressed graphically, the volume of flow plotted against the pressure will give a family of straight lines proceeding from the origin, Fig. 2, irrespective of the substance or the method of measurement.

CASE 2. VISCOSITIES ADDITIVE—EMULSIONS.—If the fluid is not identical throughout, the viscosity may yet be calculated in special cases. Take first the case of a series of vertical lamellae arranged alternately, as in Fig. 3, and subjected to a horizontal shearing stress. For convenience suppose that the lamellae of the one substance A all have the same thickness s_1 and that the lamellae of the substance B have the uniform thickness s_2, etc. Let the viscosities of the substances be η_1, η_2, . . . and the shearing forces per unit area p_1, p_2, . . . respectively, then if R is the distance between the horizontal planes, the velocity of the moving surface is

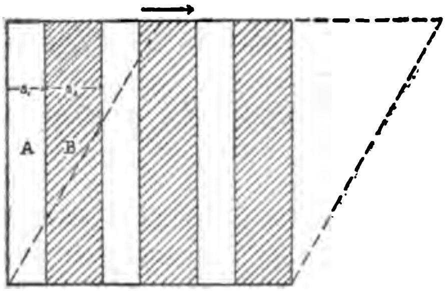


FIG. 3.—*Additive viscosities*

$$v=\frac{RP}{H}=\frac{Rp_1}{\eta_1}=\frac{Rp_2}{\eta_2}$$

where H is the viscosity of the mixture, and P is the average shearing force over the whole distance S. But

$$PS=p_1 s_1+p_2 s_2+\ \ldots .$$

hence

$$H=\frac{R}{v}\left(\frac{p_1 s_1+p_2 s_2+\ \ldots}{S}\right)$$

But since $\frac{s_1}{S}$ is the fraction by volume of the substance A present in the mixture which we may designate a, and similarly $s_2/S=b$, etc.,

$$H=a\eta_1+b\eta_2+\ \ldots\ \ldots\ldots\ldots\ldots \qquad (2)$$

This case is of particular interest in connection with emulsions. The formula tells us that the viscosity of the mixture is the sum of the partial viscosities of the components, provided that the drops of the emulsion completely fill the capillary space through which the flow is taking place.

CASE 3. FLUID MIXTURES—FLUIDITIES ADDITIVE.—If the lamellae are arranged parallel to the direction of shear, as shown in Fig. 4, we have a constant shearing stress, so that

$$P=\frac{\eta_1 v_1}{r_1}=\frac{\eta_2 v_2}{r_2}= \ldots \qquad (3)$$

where v_1, v_2, . . . are the partial velocities as indicated in the figure.

There are two different ways of defining the viscosity of a mixture, and it becomes necessary for us to adopt one of these before we proceed:

1. If we measure viscosity with a viscometer of the Coulomb, or disk, type, we actually measure the velocity v, BS in the figure, and we very naturally assume that

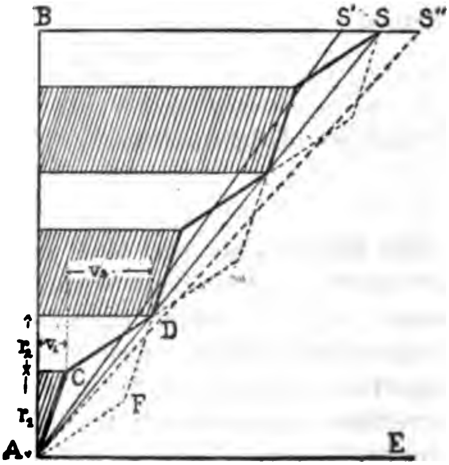


FIG. 4.—*Additive fluidities*

$$P=\frac{H\ v}{R} \qquad (3a)$$

2. It is more usual, however, to calculate the viscosity from the volume of flow, as in the Poiseuille type of instrument. Let v', BS' in the figure, be the effective velocity which the surface BS would have, were the series of lamellae replaced by a homogeneous fluid having the same volume of flow. The effective velocity is related to the quantity of fluid U passing per second in a stream of unit width, as follows:

$$U=\frac{v'\ R}{2}$$

Let the viscosity as calculated from the flow, as for a homogeneous fluid, be H', then

$$P=\frac{H'v'}{R}=\frac{2\ H'\ U}{R^2} \qquad (3b)$$

It is to be noted that had the less viscous substance been in contact with the surface AE, the effective velocity of flow would have been represented by the distance BS''. We shall take the former of these for our definition of the viscosity of a mixture, since, as we shall now show, by using it the viscosity is independent of the number or the arrangement of the lamellae.

Since

$$v=v_1+v_2+\ \ldots$$

we obtain from equations (3) and (3*a*) that

$$PR\Phi=P(r_1\varphi_1+r_2\varphi_2+\ \ldots)$$

or since

$$a=\frac{r_1}{R},\ b=\frac{r_2}{R},\ \text{etc.}$$

the fluidity of the mixture is

$$\Phi=a\varphi_1+b\varphi_2+\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

The fluidities are, according to this definition, strictly additive and entirely independent of the number and arrangement of the layers. Since, however, the viscosities are usually calculated by means of the Poiseuille formula based on the volume of flow, it is important to determine for a given arrangement of lamellæ what correction must be made to the effective viscosity, as calculated from the volume of flow, to make it accord with the true viscosity, as defined above and as obtained by the disk or other similar method for the measurement of viscosity.

Reverting again to the figure, we find that

$$\begin{aligned}U=&\frac{v_1r_1}{2}\\&+v_1r_2+\frac{v_2r_2}{2}\\&+v_1r_1+v_2r_1+\frac{v_1r_1}{2}\\&\ldots\ldots\ldots\ldots\ \ \ldots\end{aligned}$$

If there are n pairs of alternate lamellæ of the two substances A and B

$$U=\frac{1}{2}\left[n^2v_1r_1+n(n+1)v_1r_2+n^2v_2r_2+n(n-1)v_2r_1\right]\ldots\ldots(5)$$

Since $n=\dfrac{R}{r_1+r_2}$, on substituting into equation (5) the values of

v_1 and v_2, we get

$$U=\frac{R^2 P}{2}\left[a\varphi_1+b\varphi_2+\frac{ab}{n}\ (\varphi_1-\varphi_2)\right]$$

and if $\Phi'=\frac{1}{H'}$ we obtain from equation (3b)

$$\Phi'=a\varphi_1+b\varphi_2+\frac{ab}{n}(\varphi_1-\varphi_2)\ \ldots\ldots\ldots\ldots\ (6)$$ [4a]

and when $n=\infty$, the fluidity becomes simply

$$=a\varphi_1+b\varphi_2$$

and in this case

$$\Phi'=\Phi\ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (7)$$

In a homogeneous mixture it appears, therefore, that the two definitions lead to the same fluidity, and experimental results lead us to believe that this is the case usually presented in liquid mixtures, since the disk method and the capillary tube method give the same fluidity. If, however, the number of lamellæ is small, as may well be the case in very imperfect mixtures, or when the flow takes place through very narrow passages, the effective fluidity as calculated from the volume of flow may be either greater or less than the sum of the partial fluidities of the components, depending upon the order of the arrangement of the lamellæ in reference to the stationary surface. The amount to be added or subtracted from the effective fluidity in order to obtain the true fluidity is represented by the term $\frac{ab}{n}\ (\varphi_2-\varphi_1)$, corresponding to the areas *ACD*, etc., or *AFD*, etc., Fig. 4.

A combination of the cases 2 and 3 would lead to a checkerboard arrangement, but it may now be shown that such an arrangement tends to reduce to the case where the fluidities are additive.

If the arrangement considered in Fig. 3 is subjected to continued stress, the lamellæ will tend to become indefinitely elongated as indicated in Fig. 5; and unless the surface tension intervenes, as may be the case in immiscible liquids, the lamellæ will approach more and more nearly the horizontal position. Thus, so far as we

---

[4a] Dr. E. Buckingham of the Bureau of Standards has checked this derivation by another method. A more general solution has been furnished by Mr. C. A. Briggs of this Bureau.

Let N be the total number of layers. If there are m different liquids having fluidities φ_1, φ_2, φ_3, . . . and the thicknesses of the layers of each liquid are r_1, r_2, r_3, . . . respectively, the layers being arranged in this order and repeated $\frac{N}{m}$ times, the fluidity will be

$$\Phi'=a\varphi_1+b\varphi_2+c\varphi_3+\ \ldots\ +\frac{m}{N}\Big[a\varphi_1(b+c+d+\ \ldots)+b\varphi_2(-a+c+d+\ \ldots)+c\varphi_3(-a-b+d+e+\ \ldots)+\ \ldots\Big]$$

can determine without solving the complicated problem of the molecular motions, it seems certain that the fluidities will become more and more nearly additive as the flow progresses and the mixture becomes more and more nearly complete. The results of experiment verify this conclusion wherever there is no evidence of chemical union between the components of the mixture.

It has been demonstrated[5] that the viscosity of a given mixture must always be less when the fluidities are additive than when the viscosities are additive, hence the viscosity is greatest when the lamellæ are perpendicular to the direction of the shear; it is least when the lamellæ are arranged parallel to the direction of shear. But the "effective" viscosity may be made still less by placing the more fluid substance in contact with the stationary surface and having the number of lamellæ as small as possible.

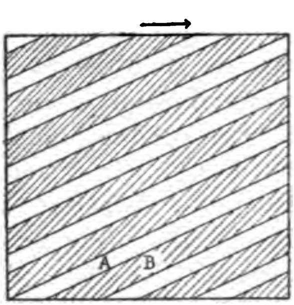


Fig. 5.—*The arrangement shown in Fig. 3 after flow has taken place. Conditions are seen to approach those of Fig. 4, so that the fluidities of a mixture tend to become additive*

Scarpa[6] has raised the important question, If the fluidities of homogeneous mixtures are additive, should there not be a mechanical separation of the components of the mixture when it is simply forced through a narrow passage, such as has never been observed? It is clear that the flow of one component *A* will cause the component *B* to be carried along, even though the fluidity of the latter may be zero. The total quantity of *A* flowing in a unit of time, regardless of whether it is derived from the fluidity of *A* or *B*, is made up of the terms of equation (5) containing r_1, and is

$$U_1 = \frac{R^2P}{2}\left(a^2\varphi_1 + \frac{n-1}{n}ab\varphi_2\right)$$

and similarly the rate of flow of the component *B* is

$$U_2 = \frac{R^2P}{2}\left(b^2\varphi_2 + \frac{n+1}{n}ab\varphi_1\right)$$

When $n = \infty$

$$\frac{U_1}{U_2} = \frac{a}{b} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (8)$$

which proves that when the number of lamellæ is large, the substance flows in exactly the ratio in which the components are present. In other words, there is no separation at all.

---

[5] Phys. Review, **35**, p. 411; 1912.

[6] Rend. soc. chim. ital. II, **5**, p. 363; 1913.

There will be a separation of the components of the mixture when the thickness of the lamellæ is great or when the passage through which the substance is forced is very small, for in either case n will be small. The separation may be calculated from the expression.

$$\frac{U_1}{U_2}=\frac{a}{b}\cdot\frac{na\varphi_1+(n-1)b\varphi_2}{(n+1)a\varphi_1+nb\varphi_2}\ldots\ldots\ldots\ldots\ldots \quad (9)$$

If the two components have the same fluidity and are present in equal proportion, the component A will flow at only one-third of the rate of B when $n=1$. Even if the fluidity of B is zero, it will flow twice as rapidly as A, under the above conditions. Since this ratio is independent of the fluidity of A, it follows that the flow of B may be increased by making the fluidity of A large.

An ingenious application of the above principle was made by the Southern Pacific Railroad,[7] when it was found that the pressure required to pump heavy oils through long pipe lines was inconveniently large. The problem was to get the maximum flow of oil for a given expenditure of work and with a given diameter of pipe. By using a rifled pipe and injecting about 10 per cent of water along with the oil, the water was thrown to the outside of the pipe by the centrifugal action caused by the rifling, and thus by a seeming paradox the water lubricated the oil, so that the delivery became from 8 to 10 times what would have been the case had the water not been added.

Similar experimental confirmation of the principle was obtained by the author as follows: Using capillary No. 1 in the viscometer we have employed above, it was found that 13 ml of pure water at 25° C under 60 g per square centimeter pressure would flow in 33 seconds. Pure cottonseed oil under the same conditions required 1640 seconds. A mixture was then made containing one-third oil and two-thirds water by volume. Had the water completely flowed through the capillary before the oil began to flow, the time of flow of the mixture should have been $22+547=569$ seconds; yet only 391 seconds were actually required, which is less than the time theoretically required for the flow of the oil alone. The difference of 178 seconds is due to the water forming a lubricating film for the oil as the water drained out of the viscometer. This effect may be regarded as a kind of "slipping."

---

[7] Engineering Record, 57, p. 676; 1908.

It is possible that under special circumstances there may be a separation of the components of a mixture even when thoroughly mixed. This would manifest itself when the capillary passages approached molecular dimensions and there was a difference in the adhesion of the components of the mixture for the surface of the passages. The component with the least tendency to wet the walls would tend to be carried along. As a matter of fact Gilpin[8] and his coworkers have found a separation of the components of petroleum in flowing through finely powdered materials.

CASE 4. SUSPENSIONS—THE SIMPLEST CASE.—The above cases apply primarily to pure homogeneous fluids, fluid mixtures, and emulsions. We come now to the consideration of suspensions of solids in fluids. In its simplest aspect we have but a limiting example of case 3, where the lamellæ of one component have zero fluidity. We have already seen that if the lamellæ were thin enough the suspension would flow without separation of the components. If $\varphi_2 = 0$, the fluidity Φ of the suspension is

$$\Phi = a\varphi_1 \dots\dots\dots\dots \quad (10)$$

that is, the fluidity of the medium will be decreased in exactly the ratio which the volume of the solid bears to the total volume of the suspension.

If, however, the lamellæ of solid B have an irregular surface, this law will not hold. If, for example, the lamellæ are pierced by numerous fine pores, the fluid will fill these pores, yet the stream lines will neither pass through the pores or be appreciably distorted by their presence. The fluidity is then

$$\Phi = (a - d)\varphi_1$$

where d is the fraction of the total volume occupied by the pores.

CASE 5. SEEPAGE.—A solid stratum placed at right angles to the direction of shear prevents all viscous flow until the pressure becomes sufficient to produce rupture, as equation (2) requires. If this stratum is pierced by one or more cylindrical pores, flow will take place and for a given area of pores it is easy to calculate from equation (1*a*) that the rate of flow will vary directly as the square of the radius of the pores. This effect of the variation of the diameter of the pores upon the rate of flow is often underestimated. If a single pore opening 1 cm in diameter in a plug be replaced by a multitude of pores with the same total area, but with a diameter of only 0.0001 cm, this being of the order of magnitude of the pores in the finest clay, then a pressure which would cause a flow of 1 cm^3 in a minute through the large opening would, according to Poiseuille's law, require 12 years to force 1 cm^3 of fluid through the small pores.

---

[8] Am. Chem. J., **40**, p. 495 (1908); **44**, p. 251 (1910); **50**, p. 59 (1913).

It is well known that compact clay is almost impervious to both water and oils, and therefore they are often associated, the the clay forming an impervious stratum through which the water or oil does not penetrate. For this reason clay is used for the cores of dams in as compact a state as possible. The fineness of the pores has an important bearing upon the penetration, retention, and circulation of water in soils. It is well known to the chemist that the rapidity of filtration increases very rapidly with the increase in the size of the grain and consequently in the size of the pores.

The fact that jellies set so as to become apparently solid substances, when only a minute fraction of the total volume is made up of true solid, is doubtless due to the formation of a connected network, which prevents the viscous motion of the jelly as a whole, and the excessively fine pores prevent the appreciable flow of the medium. It is to be expected that diffusion and electrical conduction through such a substance would be practically unimpeded, and such is the case.

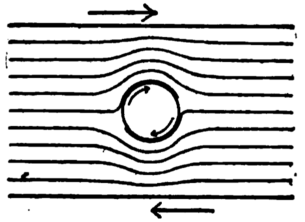


FIG. 6.—*Showing the distortion of the stream lines by the presence of a solid sphere in viscous flow. If the sphere is situated midway between the upper and lower surfaces which are supposed to be sheared with equal velocity toward the right and left, respectively, it is evident that the sphere and the stratum which would pass through its center are not moving either to the right or to the left, i. e., they have the same velocity. The figure is evidently diagrammatic only*

CASE 6. NONPLASTIC SUSPENSIONS.—A sphere suspended in a fluid of its own specific gravity, Fig. 6, is the simplest case of a suspension. The shearing of the fluid, which causes any cubical figure of the fluid to assume the form of a rhombohedron, will cause the sphere to rotate, greatly assisting the flow. The stream lines are curved on account of the presence of the sphere, but the sphere itself moves in a linear direction and with the velocity of the stratum of liquid which would, if continuous, pass through the center of the sphere.[9] Spheres in the same stratum do not tend to approach each other, since they all have the same velocity.

Spheres in different strata move with unequal velocities; hence collisions must take place, depending upon the radii of the spheres and their number per unit volume as well as upon the attraction or repulsion that may exist between them. The surfaces of two spheres which are approaching each other must be moving in opposite directions which are at right angles to the line joining their centers, Fig. 7a. The viscous resistance to this shearing action as they approach will rapidly dissipate as heat their energy of rotation.

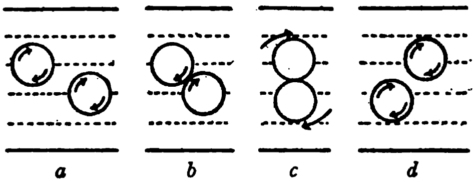


FIG. 7.—*Two spheres before, during, and after collision. The initial rotation of the individual spheres is lost on collision and this results in the dissipation of energy as heat. In the place of this individual rotation there developes a rotation of the system. It should be noted that this latter rotation causes the centers of the spheres to move in a transverse direction, indicated by the distances from the dotted lines*

The contact of two particles, which are large in comparison with molecular dimensions, brings the laws of ordinary friction into play. The spheres cannot rotate unless the torque exceeds a certain definite value, which depends upon the pressure existing normal to the surfaces at their point of contact, and this pressure in turn depends not only upon the rate of shear but on the attraction or repulsion which may exist between the spheres.

When two spheres come into contact, Fig. 7b, they must remain in contact for a definite period. If the spheres were without

---

[9] Einstein (Ann. der Physik, **19**, p. 289, 1906) and Hatschek (Kolloid-Zeitschrift, **7**, p. 301, 1910; **8**, p. 34, 1911; Trans. Faraday Society, March, 1913) have both considered the case of suspensions of spherical particles at low concentrations. They both arrive at a formula

$$H=\eta_1\,(1+k\,b)$$

or

$$\Phi=\frac{\varphi_1}{1+k\,b}$$

where *b* is the volume fraction of solid present and *k* is a constant for which Hatschek deduced the value of 4.5 and Einstein of 1. The formula is hyperbolic in form, while the fornula, equation (12), obtained by Bingham and Durham experimentally, and confirmed by the experiments of Oden (Zeitschr. f. physik. Chem., **80**, p. 709, 1912) is linear.

There is a slip in Hatschek's reasoning. He says: "It is obvious that the liquid at the upper pole of each spherical particle moves with a somewhat greater velocity than at the lower pole, which is equivalent to a translatory movement of the particles with a velocity equal to half the difference of the two velocities prevailing at the two poles." He thus neglects entirely the rotation of the spheres and assumes that they are moving faster than the stratum of fluid which would pass through the centers of the spheres. That these two motions are equivalent is at least not self-evident. His formula is obtained by the employment of Stokes's formula for a sphere moving through a viscous medium without rotation.

It is worth noting that if their formula held at high concentrations the pure solid would have a fluidity of 18 per cent (Hatschek) to 50 per cent (Einstein) of the fluidity of the continuous medium, irrespective of the nature of the medium. This result is of course absurd. We believe that it shows that the values obtained by the use of the formula will always tend to be higher than the values found experimentally.

attraction or repulsion for each other, they would become separated as soon as their centers had come to be in the same vertical plane, Fig. 7c.

The spheres cannot rotate as individuals unless the torque exceeds a certain minimum value, which depends upon the pressure which exists normal to the surfaces in contact. Seepage can take place at low rates of shear, but we are here considering the flow of the mass.

During the time of contact of two spheres they rotate as a whole and pass out of the strata of liquid to which they formerly belonged, Fig. 7c, and into strata of widely different velocities. During this period of acceleration the liquid will flow around the spheres and through the interstices between them. Thus, other spheres tend to collide with those already in contact, after which the combined mass tends to rotate as a whole. When equilibrium is reached these clots will have a certain average size, depending upon the number, size, and specific attraction of the particles.

For the present purpose, the important thing to observe is that as these clots increase in size and number there comes a point when the clots come in contact across the entire width of the passage. At this point viscous flow stops and plastic flow begins.

For a given substance and volume concentration, the number of collisions will be proportional to the number of particles which varies inversely as the cube of the radius. But if the angular velocity is independent of the radius, the energy of rotation will vary with the square of the radius, hence the loss of energy, due to collisions, will be inversely proportional to the radius.

Experiment proves that the viscous flow of suspensions follows the law[9a]

$$\Phi = \left(1 - \frac{b}{c}\right)\varphi_1 \qquad (12)$$

where b is the concentration of solid by volume and c is the particular value of b at which the fluidity of the suspension becomes zero. The value of c can vary only from 0 to 1, the value increasing with the size of the particles. When $c = 1$ the formula becomes the same as in Case 5, $\Phi = a\phi_1$ where no collisions are taking place. This perhaps indicates that the decrease from unity in the value of c actually found is due solely to collisions.

CASE 7. PLASTIC SUSPENSIONS.—We have supposed that the stress is insufficient to overcome the friction between the particles.

[9a] Phys. Review, 35, p. 423; 1912.

If the stress is sufficient to cause the surfaces to slip over each other, a flow will result which must be regarded as plastic in its nature, since a certain definite stress is required for its production. It is evident that the friction must increase as the number of continuous chains of particles across the passage is increased.

There is a superior limit to the volume concentration of solid in this type of plastic flow. If the solid phase is made up of spheres of equal size, no further concentration is possible after the spheres are closely packed. As soon as this becomes the case, movement among the particles is prevented and the only flow possible is by slipping at the boundary or at a surface of rupture, and of the medium filtering through the interstices. There are two methods of closely packing spheres, the tetrahedral packing with a pore space of $1-\frac{\pi}{3\sqrt{2}}$ or 25.96 per cent by volume and the cubical packing with a pore space of $1-\frac{\pi}{6}$ or 47.64 per cent by volume. Since the pore space is independent of the radius of the particles, and since interlocking of the spheres occurs as soon as the pore space becomes less than 47.64 per cent, the concentration of solid corresponding to this pore space appears to be the maximum concentration for the occurrence of plastic flow of the first type, and at this concentration of 52.36 per cent slipping must take place if the mass is to flow as a whole.

While the maximum concentration for plastic flow is thus independent of the size of the particle, we have seen that the concentration at which plastic flow begins decreases with the decreasing radius of the particles. To have a considerable range of plasticity, the spheres must therefore be very small. It is this fact which is of fundamental importance in the study of plastic substances.

What has been stated above in regard to the effect of piercing the lamellae with fine pores may be extended to the case where the particles are porous spheres or bodies with reentrant angles or other irregular outline.

If the view here presented is correct, the point where plastic flow begins is independent of the viscosity of the medium, so long as the attraction or repulsion between the particles is the same. For example, in dry clay the medium filling the pores is air. When the clay, thoroughly worked to separate the particles from each other, is put into a receptacle and shaken down thoroughly, the particles evidently move—not with perfect freedom as in a viscous fluid—but rather as a plastic substance, bridging across the space so that the packing is by no means the closest possible. In an actual experiment, after continued shaking for about a half hour, the pore space, as determined by means of carbon tetrachloride, was not 47.64 per cent as with equal spheres and close cubical packing but 81.6 per cent by volume. In an aqueous suspension made with water containing one-tenth of 1 per cent of potassium carbonate the plastic flow was found to begin in a mixture containing 80.5 per cent water by volume.

IV. DISCUSSION OF EXPERIMENTAL DATA

1. LAW OF PRESSURES

We take the data for capillary No. 1, Table 2, Fig. 8, to prove that for a certain medium range of pressures the volume of flow is quite accurately represented by the formula

$$v = K\ (P - f) \qquad (13)$$

where v is the volume of flow per second, f is what we shall denominate the friction constant[10] expressed in grams per square centimeter required to start the flow and determined graphically as the intercept of the volume-pressure curve on the pressure axis as shown in Fig. 8, and K is an arbitrary constant. To test the formula the values of K are given in Table 14.

TABLE 14

No.	P−f	$v \times 10^3$	$K \times 10^6$	Deviation from mean
20	48.8	5.53	116.0	− 0.9
19	50.6	6.14	120.3	+ 3.4
2	76.6	9.06	118.2	+ 1.3
1	78.5	8.95	114.0	− 2.9
7	100.1	11.82	118.1	+ 1.2
3	113.0	9.17	81.1	....
8	128.1	14.37	112.0	− 4.9
9	128.8	15.49	120.3	+ 3.4
11	156.7	19.97	127.4	+10.5
10	157.2	17.66	112.3	− 4.6
4	210.0	23.23	110.6	− 6.3
Av.....	....	....	116.9	3.9

---

[10] The term "internal friction" is used sometimes as synonymous with viscosity. There is not only no need for this term but there is positive objection to its use in this connection, since the laws of viscous flow are quite different from the laws of ordinary friction. Since in suspensions we have the collisions of particles with the dissipation of the energy of translation according to the laws of friction, we have here a true internal friction, and it seems best to reserve the use of the term for this case.

Leaving out experiment No. 3, which appears to be grossly in error, we obtain an average value for K of 116.9, with an average deviation from this mean value of 3.9. There is no perceptible drift in the mean value when the experiments are arranged as here in their order of increasing pressures or in their chronological order.

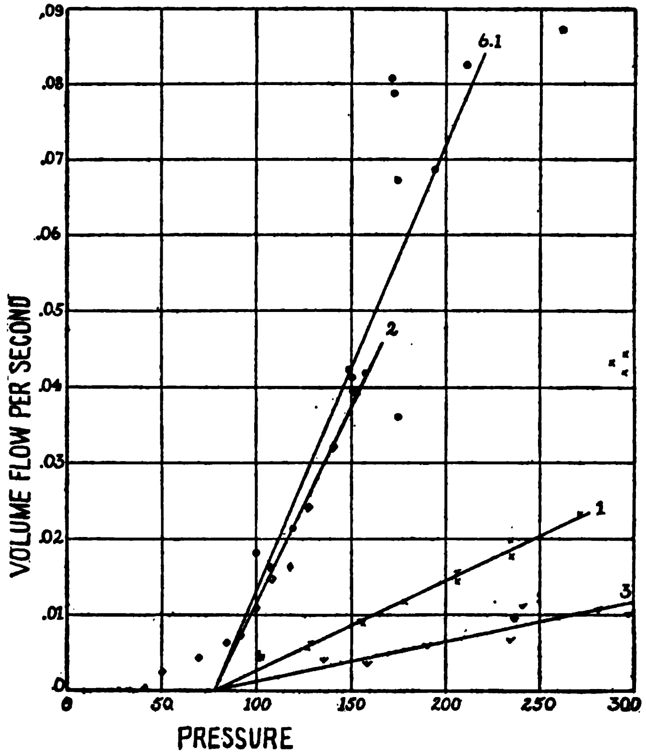


Fig. 8.—*The results of experiments at 25° C with Capillaries No. 1, No. 2, No. 3, and No. 6.1 with 50 per cent by weight of clay suspended in pure water are here plotted. For medium pressures the curves are linear and intersect each other at a point on the pressure axis which is widely removed from the origin. Comparing this with Fig. 2, we see that this affords a sharp distinction between viscous and plastic flow. Capillary No. 1 shows that at high pressure the flow suddenly increases, which is believed to be due to slipping. Capillary No. 2, shows that there may be an increased flow at low pressures, which is probably due to seepages*

If the above law held at all pressures, no flow would occur at pressures less than that equal to the friction constant. Experiments with capillary No. 2 in particular demonstrate that flow does, however, take place below this pressure.

We believe that this flow is of a different character from the flow at the pressures just considered, and that it is associated with a change in concentration due to seepage. Certain it is that even were there no flow en masse, there must of necessity be more or less seepage through and around the material. Such seepage would be a maximum in mixtures with low concentration of solid, since this would increase the size of the pores, and with pressures which are nearly sufficient to cause the flow of the mass as a whole. As this seepage takes place we have noticed, under unusual circumstances, almost pure water flowing out, but very slowly. More usually the seepage causes a change of concentration of the part entering the capillary; this in turn causes a lowering of the friction constant, and consequently the material flows en masse with a minimum of separation but with considerable velocity.

But the question arises, Will there not be seepage even when the pressure is more than sufficient to overcome the friction? Table 15 gives an affirmative answer to this question, but it also indicates that the conditions of flow are unstable, since the values of K vary widely even when the pressure is practically constant. The percentage of clay in the mixture, which had flowed through the instrument and was found by analysis, is given in the last column of the table and serves as an indication of the amount of change in concentration of the original 50 per cent mixture due to seepage.

TABLE 15

No.	P−f	$v \times 10^3$	$K \times 10^6$	Per cent clay by analysis
13	2.1	2.45	1165	49.2
18	23.4	4.48	191.3	48.7
14	23.8	5.00	210.0	....
15	24.3	4.90	201.9	....
16	24.9	4.21	169.0	....
17	25.3	4.50	177.8	....

At high pressures there is also an increase in the rate of flow, but unlike the increase at low pressures it takes place suddenly. Comparing table 16 with table 14, we see that increasing the value of $P-f$ from 192.9 to 210 causes an increase in the value of $K \times 10^6$ from 120 to 209, and the values at still higher pressures are in the region of this higher value.

TABLE 16

No.	P—f	$v\times10^8$	$K\times10^6$
5	210.0	43.84	208.8
12	216.3	41.94	193.9
6	217.3	44.87	206.5

From the first it has been apparent that this phenomenon can not be ascribed to experimental errors. It appears repeatedly in the course of this investigation and the phenomenon was somewhat thoroughly investigated when using capillary No. 6.3 and an alkaline suspension. (See Table 7, Fig. 9.)

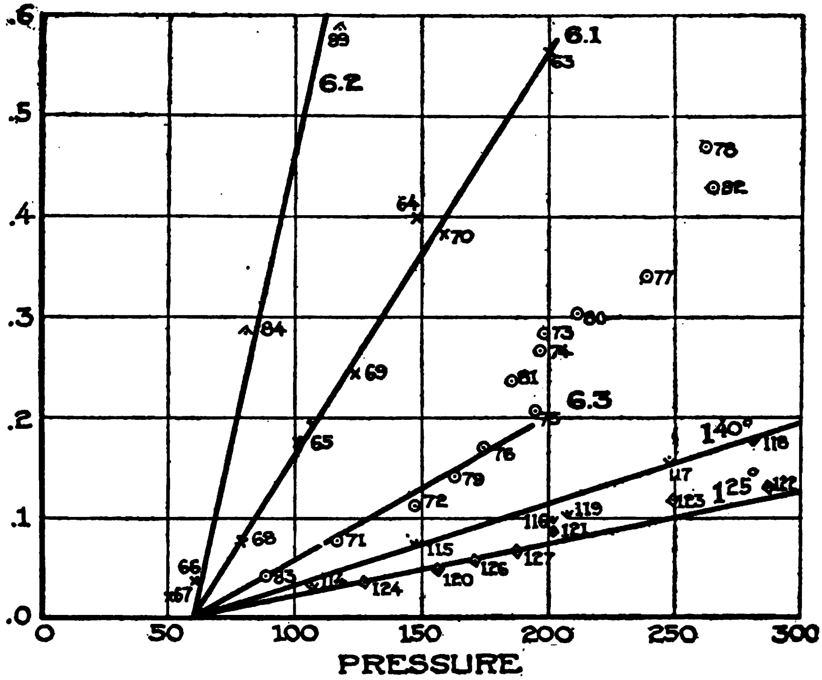


FIG. 9.—*The results of experiments at 25° C with Capillaries No. 1, No. 6.1, No. 6.2, and No. 6.3 with 50 per cent by weight of clay suspended in a 0.1 per cent solution of potassium carbonate, and with Capillary No. 1 at 40° C, are here plotted. The friction constant is less and the mobility far greater than in the neutral suspension. Rise in temperature increases the mobility. With Capillary No. 6.3 the results are irregular at high pressures*

It occurs to one at once that in fluids there is a change from viscous flow to hydraulic flow as the velocity increases and reaches a certain critical value. However, it is extremely improbable that this change in régime is due to the eddies which cause hydraulic flow, because the total kinetic energy of the material flowing through the capillaries in our experiments formed a negligible part of the total energy expended. This is shown in column 7 of Tables 2 to 14. The probable cause will be discussed later.

From our analysis of the data for capillary No. 1 given in Table 2, we conclude that the law of pressures expressed by equation (13) holds true for medium pressures, but not for high pressures nor for pressures only slightly greater than the friction constant. This conclusion is confirmed by later experiments, as may be judged from the value of μ in the Tables 2 to 14.

2. FRICTION CONSTANT

The friction is constant to within the limits of experimental error for suspensions in neutral solution, as shown by capillaries No. 1, Table 2; No. 2, Table 3; No. 3, Table 4; and No. 6.1, Table 5. Capillaries 1, 2, and 3 differ from each other very little in diameter but considerably in length, No. 3 being 3.6 times the length of No. 2. Yet the friction is 78 for both. This proves that the friction is independent of the length of the capillary. On the other hand, the radius of capillary No. 6.1 is over twice that of the others. Since its friction is the same, it follows that the friction is independent of the radius of the capillary.

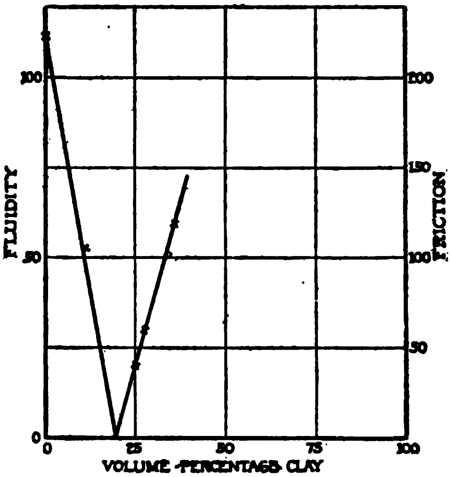


FIG. 10.—*As the volume percentage of clay is increased the fluidity rapidly decreases and becomes zero in the 19.6 per cent mixture. At this concentration the friction begins to have a positive value and increases rapidly and in a linear manner, equation (14)*

We should expect that decreasing the pressure between the solid particles would also decrease the friction. Hydroxyl ions are well known for their deflocculating power and accordingly the friction in the alkaline solutions is less than in those which are neutral, the friction dropping from 78 to 59.5 in the very weakly alkaline solution used. The experiments with capillaries No. 1, Table 13; No. 6.1, Table 6; and No. 6.3, Table 7, give a value for the friction which is 59.5 to within the experimental error, for 50 per cent suspensions at 25°. Experiments made with the same suspension at 40° using capillary No. 1, Table 12, give the same friction. This indicates that the friction is independent of the viscosity of the medium.

The value of the friction varies rapidly as the concentration of the suspension is altered, Fig. 10, but in a linear manner as expressed in the following formula:

$$f' = (b - 0.196)\ 718 \qquad (14)$$

The values of f and f' are given in Table 17.

TABLE 17

Fraction solid by volume—b	Friction constant observed—f	Friction constant calculated—f'
0.2528	40.0	40.8
.2762	59.5	57.6
.3640	119.0	120.6

3. MOBILITY

Given the law of pressures, we may make the assumptions made in regard to viscous flow and derive the formula, quite similar to equation (1*a*)

$$\frac{1}{\mu} = \frac{\pi g r^4 t (P - f)}{8V\,(l + \lambda)} - \frac{m\rho V}{8\pi\, t(l + \lambda)} \qquad (15)$$

For a given capillary

$$\frac{1}{\mu} = C\, t(P - f) - C'\rho/t \qquad (16)$$

where C and C' are constants.

In Tables 2 to 10 the values of the last two terms in equation (16) are given in columns 6 and 7, and the values of μ, to which we refer as the mobility,[11] are given in the last column of the tables.

In Table 18 we summarize the data in reference to the mobility.

---

[11] The term "mobility" has occasionally been used as synonymous with fluidity, but for this use it is unnecessary. For the purpose for which it is here employed it is closely related to fluidity but not identical with it.

TABLE 18

Table	Cap. No.	Suspension [a]	Temp., °C	$K\times10^8$	Length	μ	μl
3	2	50 neutral	25	508	1.2195	2.48	3.02
2	1	50 neutral	25	117	2.4680	1.17	2.89
4	3	50 neutral	25	56.3	4.4120	1.02	4.50
5	6.1	50 neutral	25	602	5.0110	0.73	3.66
13	1	50 alkaline	25	521	2.4680	5.11	12.61
8	6.2	50 alkaline	25	....	2.5094	<7.4	<18.5
6	6.1	50 alkaline	25	4012	5.0110	4.60	23.05
7	6.3	50 alkaline	25	1462	9.9983	3.37	33.7
11	1	47 alkaline	25	....	2.4680	7.35	18.1
13	1	50 alkaline	25	521	2.4680	5.11	12.61
9	6.2	60 alkaline	25	....	2.5094	0.119	2.99
10	6.2	70 alkaline	25	0	2.5094	0	0
13	1	50 alkaline	25	521	2.4680	5.11	12.61
12	1	50 alkaline	40	766	2.4680	7.88	19.4

[a] The suspensions are expressed in terms of percentages by weight of clay.

From the above table it is clear that the mobility is not constant for the different capillaries, even though the material is identical, but it decreases as the capillary is lengthened. In fact, for the suspensions in pure water, the product of the mobility and the length, given in the last column, yields a much more nearly constant quantity. This taken by itself would indicate that the law of lengths, which holds for viscous flow, does not hold for plastic flow. The data seem to indicate that the volume of flow varies inversely as the *square* of the length of the capillary. However, on closer examination of the data, we find that this can not be the true explanation.

In the first place, the value of the mobility for the alkaline solutions is more nearly constant than is the product of the mobility and the length of capillary, which proves that the volume of flow apparently varies inversely neither as the first nor second nor any fixed power of the length.

In the second place, we recall that at high pressures capillary No. 1 in 50 per cent neutral suspension gave a much higher rate of flow, corresponding to a mobility of about 1.98, which is nearly twice the value taken for the average, or 1.17. Similarly capillary No. 6.1 gave one value as high as 1.63, and on the other hand, capillary No. 2 gave one value as low as 1.92. Now these divergences in our values are far outside of any known error in measurement and we can explain them only by assuming a change of régime in the case of the higher values. We will discuss the nature of this new régime later.

We therefore return to the provisional acceptance of the laws of lengths and diameters for plastic flow which hold for viscous flow and leave for future work the elimination or estimation of the extraneous influence on the flow which is here apparent. (See "Slipping," p. 340.)

Since the mobilities which we have obtained for the suspensions of different concentrations are for capillaries of practically the same length, we may regard the results as truly comparable, although the absolute values may be subject to correction.

In Fig. 11 we have plotted mobility against volume concentration. The curve begins with a very large value at the 19.6 per cent suspension by volume, decreases rapidly and reaches a very small value at about 40 per cent of solid. The curvature is very great near this latter concentration, and it is therefore critical as regards the character of the flow. We noted a marked change of appearance as this concentration was passed. In all of the lower concentrations the surface tension was strong enough to cause the material flowing from the capillary to take the form of drops, but in the higher, 47 per cent, suspension, the material for the first time flowed out in the form of a wire.

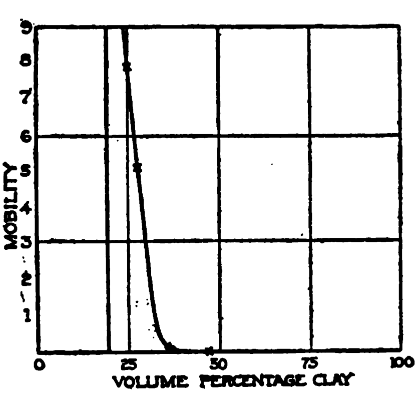


FIG. 11.—*The mobility decreases very rapidly from the 19.6 per cent mixture, where the fluidity is zero, and the mobility a maximum to a 50 per cent mixture where the mobility is negligible on the scale used*

The region of notable mobility is therefore very restricted, even in a very plastic clay. In a so-called "nonplastic" substance, this curve would doubtless be very much steeper. It is also evident that at still higher concentrations of solid than those used here, the flow must be very slight for moderate pressures or else slippage must play an important part. We know that in technical practice, slipping of the type discussed earlier under case 3 is definitely promoted by wetting the die through which the material is forced with some substance having considerable fluidity.

The effect of a 0.1 per cent alkali upon the mobility is even more marked than upon the friction constant, the mobility being raised from 1.17 to 5.11, both suspensions being measured in capillary No. 1. There is then an increase of over 330 per cent, which is a truly extraordinary effect.

The temperature has an effect upon the mobility which is only less marked than that just considered, but the increase in the mobility as the temperature is raised is readily accounted for by the increase in the fluidity of the medium. The ratio of the mobilities is

$$\frac{\mu_{40^\circ}}{\mu_{25^\circ}}=\frac{7.88}{5.11}=1.54$$

while the ratio of the fluidities of water at these temperatures is

$$\frac{\varphi_{40^\circ}}{\varphi_{25^\circ}}=\frac{166.9}{111.7}=1.49$$

The difference between these is a little over 3 per cent, which is easily accounted for on the basis of experimental error.

It seems appropriate to conclude this section with some remarks of a general nature upon mobility and its relation to plasticity.

Any substance which requires a shearing stress of finite magnitude to produce a permanent deformation without rupture is plastic. If infinitesimal stress is sufficient to produce permanent deformation, the substance is viscous. All liquids and gases are viscous, and all plastic substances must be regarded as solids.[13] It does not follow that all solids are plastic, for if on subjecting a body to shearing stress all of the deformation is temporary, the body is perfectly elastic and nonplastic for the stress under consideration. If, on increasing the stress, rupture takes place before there is any permanent deformation, the substance is brittle and totally nonplastic. If the space between two parallel planes at unit distance apart is filled with a plastic substance, and a unit tangential force per unit area be applied in addition to the force required to just overcome the friction, the velocity given to either plane in respect to the other is a measure of the mobility.

We have hitherto avoided the term "plasticity." The conception underlying the word is not only of capacity of a substance for being molded into a desired form, but necessarily of retaining that form when it is once attained. Plasticity is therefore not a simple property. We have seen that the ability of a substance for taking a desired form is dependent upon the mobility and perhaps the slipping, and also upon the friction constant. It is a maximum when the friction is zero and the mobility a maximum. On the other hand, the ability of a substance to hold its form is dependent primarily upon the friction constant, but the rate of change of form is dependent upon the mobility. It is a maximum when the friction constant is a maximum and when therefore the mobility is very small.

---

[13] Throughout this paper we use the term "fluid" as synonymous with "viscous substance," and the term "solid" as synonymous with the term "plastic substance." We hope later to study the flow of emulsions, foams, metals, etc. At present we are not prepared to discuss these types of flow.

It is sometimes desirable to strike a balance between the two factors of ease of working and stability of form which is suited to the given conditions. In paint the mobility must be high and the friction may be low, but in pottery material it is necessary that the friction constant be relatively high. As the friction is increased the concentration is finally reached where the pore space is no longer filled with liquid. The material then loses cohesiveness and crumbles.

In the comparison of plastic materials it would appear that the ratio of mobility to friction would have practical importance, but perhaps more important still is the slope of the mobility and friction concentration curves or the range of concentrations between the one in which the friction is zero and the one in which the mobility is negligible.

4. SLIPPING

If the shearing stress exceeds a certain value rupture takes place, quite independent of whether the material is a viscous fluid like pitch or a plastic solid like steel or soft lard. In a heterogeneous mixture like clay suspensions the conditions at the boundary, or slight local changes in concentration, may be the cause of further separation of the solid from the liquid medium, giving rise to the slipping already discussed under case 3, the water forming the lubricating layer. Slipping has never been positively identified in the flow of liquids even after the most painstaking search, but there is no inherent reason why the phenomenon should not appear in plastic flow where the force required is so much greater. We should expect to detect it when the pressure becomes very great or, what is practically the same thing, when the capillary is very short, making the pressure gradient large. It is precisely under these conditions that our experiments give unexpectedly large values for the flow.

In our experiments the unexpectedly large values appeared very suddenly with increasing pressure. Whether or not there are really two curves with a metastable region where they join is not clear at present, but it seems likely that the high values do not fall on a smooth curve.

V. RELATION OF RESULTS TO EARLIER WORK ON PLASTICITY

There are doubtless many types of plastic substances, but for practical reasons the plasticity of clay has received the most attention. Doubtless, however, the observations made in regard to clay have a general application.

In explaining why some clays are plastic and others are not fineness of grain must play the most important rôle, if the views presented in this paper are correct. Fineness of grain alone brings about certain effects which are important.

1. Fine grains result in fine pores when the particles are close together, but water diffuses very slowly through such a material. In a pile of wet sand the water diffuses rapidly and thus the lower portions become weak because of too much water while the upper portions may be crumbling from having too little.

2. Fine-grained material has a far greater pore space than coarse-grained material in the concentration which has zero fluidity and zero friction. There is therefore a greater range of concentrations over which the material is plastic.

3. For a given value of the friction the fine-grained material will contain more of the liquid medium than will a suspension of coarser particles. This greater percentage of water will naturally increase the mobility and the slipping. But since for a given friction the pore space, and therefore the water required to produce plasticity, is greater, we should expect shrinkage on drying. Since, moreover, the diffusion of the water outward will be very slow in the finest material, we should expect that unless the drying is accomplished very slowly the shrinkage would be accompanied by cracking.

4. On drying, the fine-grained material will offer more numerous points of contact between the particles over a given cross section. This will result in a stronger cohesion. The finer the material the more rapidly will salts dissolve out of it. This possible increased concentration of salts, and the fact that there is an increased volume of solution due to the large pore space, makes the amount of cementing substance larger in the fine-grained material.

5. Owing to the slow diffusion through the fine material the medium will tend to become highly concentrated with soluble substances. Furthermore, liquids passing through the fine material will tend to leave behind their larger particles or molecules.

Possibly in this way we may explain the high adsorption and hygroscopicity of plastic clays.

All of the above consequences of fineness of material are found in plastic clays which have been investigated. There are, however, numerous exceptions when we attempt to get anything like a quantitative relation. Since there are several other important variables besides the size of grain, exceptions are to be expected. The theory would lead us to expect that the shape of the grain would have an important bearing upon the plasticity. Furthermore, the size of grain is not easily determinable because the grains are usually of varied sizes. We have already seen that the mobility is affected in a marked degree by the alkaline or acid character of the medium and it may also be dependent upon the specific cohesion between the particles. Moreover, the mobility is dependent upon the fluidity of the medium. This, in turn, is affected by temperature and by substances in solution, either crystalloid or colloid.

For our present purpose it will be sufficient if we show that fineness is the prime factor in producing plasticity. It has been more than suspected for a long time that fineness is a cause of plasticity, but the reason for such a connection has not before been pointed out.

First of all clay, so well known for its plasticity, is not a definite substance. In the mechanical analysis of soils the very *fine* material is called clay regardless of its chemical composition. Merrill[13] says, in criticism of the current definition of clay—

> Kaolinite is itself not properly a clay nor is it plastic. Further, in many cases it is present only in unessential quantities. More open to criticism yet, because more concise, is the statement sometimes made that clay is a hydrated silicate of alumina, having the formula $Al_2O_3.2SiO_2+2H_2O$. It is doubtful if a clay was ever found which could be reduced to such a formula excepting by a liberal use of the imagination. There is scarcely one of the silicate minerals that will not when sufficiently finely comminuted yield a substance possessing those peculiar physical properties of unctuous feel, placticity, color, and odor which are the only constant characteristics of the multitudinous and heterogenous compounds known as clays. Daubree, as long ago as 1878 (Geologie Experimentale 1879, p. 25), pointed out the fact that by the mechanical trituration of feldspars in a revolving cylinder with water, an impalpable mud was obtained which remained many days in suspension, and on drying formed masses so hard as to be broken only with a hammer, resembling the argillites of the Coal Measures.

Grout[14] states that "All finely ground substances show this property of plasticity to a greater or less extent." The experiments of Rosenow[15] on the hygroscopicity, heat of wetting, and size of grain point to an enormously increased surface in plastic clays. Wheeler[16] has found that nonplastic slates, Iceland spar, propyllite, gypsum, and hallosite can all be made to show apparent plasticity. Stull[17] found that mica ground for 15 hours with water and then screened to 120 mesh "developed a surprising degree of plasticity; in fact, it showed a greater degree of plasticity than some clays which are being worked successfully at the present time. This tends to prove that plasticity in kaolinite is due to fineness of grain and thin plate-like structure." (Cf. also Vogt[18].)

---

[13] Nonmetallic Minerals, Wiley and Sons, p. 221; 1904.

[14] W. Va. Geol. Surv., 3, p. 38; 1906.

[15] Ton-industrie Zeitung, 35, p. 1261; 1911.

H. B. Fox[19] in the ceramic laboratories of the University of Illinois, separated the grains of a shale and a glacial clay into the several grades of fineness and found that all the grades possessed a plasticity that varied directly with the fineness of the grain, and that the coarse grains which could not be disintegrated by 20 hours of constant shaking in water, when broken down in a mortar, developed plasticity that increased as the size of the grains decreased, until when the coarse grains had been reduced to an impalpable powder they developed a plasticity nearly equal to that exhibited in the finest grains that had been separated from the original sample, showing, it is believed, that the coarser grains were comprised of minerals similar in every respect to those in the fine grains, but cemented in such a way that they withstood successfully the disintegration treatment.

According to Ladd,[20] clays can be divided into three classes, as follows:

> (1) Those which occur in their place of origin—that is, indigenous clays, which consist of plates, variously aggregated, and prismatic crystals; (2) those which have been transported, broken into cleavage scales, and deposited in degrees of fineness, according to the sorting power of water, moving with different rates of flow; and (3) those which have been indurated either by cementation, recrystallization, or some unknown cause, to the point where they will no longer slack in water. In order to make the clays of the last class plastic, they must needs be first ground. The other two clays are both plastic, the former the least so; while of the latter those which are the finest in grain having been carried the farthest or deposited in the quietest water, are the most plastic of all. These clays differ, respectively, in a marked degree of plasticity according to the amount of interstitial water which they contain. A certain percentage of the latter, differing in the different clays, gives a maximum plasticity.

Johnson and Blake[21] say, "Plasticity is a physical characteristic and appears to have a close connection with the fineness of the particles." Bleininger[22] remarks that in certain clays "a close and dense structure prevails which does not absorb water until the latter is forced into the pores by grinding and pugging. Clays of this type therefore show but a feeble initial plasticity. * * * It seems to be a fact that plasticity as measured by the ability of the clay to be molded and to flow through dies is dependent upon the development of this water-saturated micellian structure."

---

[16] Missouri Geol. Survey, 4, p. 97; 1896.

[17] Trans. Amer. Ceram. Soc., 4, p. 255; 1902.

[18] Ton-industrie Zeitung, p. 140; 1893.

[19] Purdy, Ill. State Geol. Surv. Pull., 9, p. 182; 1908.

[20] Georgia Geol. Surv. Bull., 6a, p. 29; 1898.

[21] Amer. Jour. of Science, 2 ser., 98, p. 351; 1867.

Even when the particles of clay are not cemented together there is no reason for their becoming separated from each other spontaneously merely by the presence of water, which at best can only diffuse very slowly through the pores that exist. Yet in order to develop the mobility of the material the close packing must be destroyed and the pores opened up. To effect this, mechanical force must be employed. Thus, there comes about the importance to the ceramist of kneading in the pugging mill, or wetting and drying, and particularly of freezing and thawing.

Grout[23] found that all of the clays tested by him were improved in plasticity by alternate wetting and drying. "Shales ground to 40 mesh weathered to approximately the same figures as the duplicates at 100 mesh. This suggested that the action might be largely mechanical. The amounts of clay (below 0.005 mm) in shale No. 63 were determined before and after weathering. The per cent rose from 7.7 to 17.8 by one wetting and drying."

Rolfe[24] states: "When beds of kaolin or of flint clay * * * are exposed to the action of the weather for a sufficient length of time disintegration takes place and the nonplastic material becomes plastic." (P. 28.) Speaking of the minerals in kaolin, he says: "Admixtures of these minerals when pure form a white mass, pulverulent or easily made so by weathering, and but little plastic until finely ground, but its lack of plasticity is probably due to cementation of its grains." (P. 27.) He says of flint clays: "There is a class of clays of almost stony hardness having a conchoidal fracture and a structure so like flint that they are commonly known as flint clays * * *. There is then no necessary relation between the flinty structure and their chemical composition or any physical property except plasticity. All flint clays are nonplastic. Some are rendered more or less plastic by the ordinary grinding and kneading to which clays are subjected, but some are not." (P. 31.) Speaking of gumbo clays, he says: "These are composed of exceedingly fine clay-like material which packs so closely that water passes through it but slowly. It was laid down in still water, the streams which brought it having deposited all sediment coarser than the finest sand and clay, because of loss of velocity, before reaching this point. It is very plastic and possesses great binding power, but dries slowly and cracks badly." (P. 34.)

---

[22] Bureau of Standards Technologic Paper No. 1, p. 3.

[23] Loc. cit.

[24] Illinois State Geol. Surv. Bull., 9, p. 28; 1908.

Beyer and Williams[25] state: "Although pure clays, which consist alone of kaolinitic grains are commonly nonplastic, they frequently possess plasticity or may be made to exhibit this property by pulverization and weathering and without any alteration of their composition."

Finally, it may be noted that in adding sand or other nonplastic material to plastic clay the plasticity is lowered less in proportion as the material added is finely divided.

There is at present no reliable means for measuring plasticity. It has been proposed to measure various other properties instead which are supposed to be related to plasticity, such as the amount of water required to bring the clay to a proper consistency, the tensile strength of the wet clay or of the clay after drying, of the adsorptive power of the clay for certain dyes such as malachite green, of the shrinkage on drying, or of a combination of such tests. That there is a relation between plasticity and these other properties is thus generally recognized. Thus Purdy[26] states: "Experimental evidence indicates that variation in the fineness of grain controls many of the physical and pyrochemical properties exhibited by clays. Plasticity, shrinkage in drying and burning, tensile strength, drying properties, rate of oxidation, rate of vitrification, toughness of burned ware, and, finally, to some extent, pyrometric value of the clay, are all influenced by fineness of grain."

The following table is compiled from the work of Purdy. In column 1 are given the names of the clays; column 2 shows the relation between the amount of surface in a unit volume for the different clays; column 3 gives the percentage by weight of dry clay particles of diameters ranging between zero and 0.001 mm; column 4 gives the average volume shrinkage in percentage; column 5 gives the amount of water needed to produce maximum plasticity, while column 6 gives the excess of water over and above that required to fill the pores of the dried brick; column 7 gives the maximum tensile strength in kilograms per square centimeter. If we multiply the figures in column 8 by 10^{12} we get an idea of the number of particles in 1 gram of some of the clays used.

---

[25] Iowa Geol. Surv., 14, p. 89; 1904.

[26] Illinois State Geol. Surv. Bull., 9, p. 149; 1908.

TABLE 19

Relation Between Fineness of Grain, Columns 2, 3, and 8, and Shrinkage on Drying, Column 4, Percentage of Water, Column 5, Excess of Water Required to Produce Maximum Plasticity over that Required to Fill the Pores, Column 6, and the Tensile Strength, Column 7

1	2	3	4	5	6	7	8
H 21	783	34.67	18.0	18.0	7.8	9.16	1940
H 23	634	27.30	20.4	21.4	10.3	23.41	1589
K 10	604	25.52	18.3	19.6	8.4	13.24	....
H 20	553	23.97	16.5	18.3	8.0	8.21	....
K 4	514	22.24	10.1	16.27	3.6	10.81	....
I-II	489	21.40	....	14.4	6.4	13.74	....
H 18	444	19.22	....	....	....	7.21	....
K 12	403	15.32	12.7	13.35	5.7	12.97	....
R 1	397	15.53	13.9	13.4	5.5	11.11	....
G 21	366	15.72	....	....	....	9.25	....
K 13	356	13.15	10.5	16.3	3.6	8.35	....
K 32	341	13.96	10.5	16.82	5.4	9.93	794
K 2	331	13.90	12.2	16.77	4.8	12.29	829
K 11	339	12.94	13.5	....	....	9.52	....
K 7	300	11.81	9.6	17.57	4.9	6.98	....
R 3	291	11.79	....	....	....	5.22	....
K 5	287	11.43	5.2	13.06	1.8	5.71	....
R 4	275	10.85	6.1	13.2	3.9	5.36	....
K 8	262	10.05	7.5	14.4	3.3	5.36	....
K 1	256	9.76	6.2	14.9	3.3	7.35	560
K 14	254	9.67	6.1	13.6	2.5	6.71	....
K 6	221	7.77	10.1	17.03	3.8	8.16	440
K 9	195	7.63	3.5	13.4	1.9	4.37	....

Since the values in columns 2 and 3 are quite closely parallel, either may be taken as a measure of the fineness of grain. There is certainly a very definite relation between fineness of grain and the amount of water in excess of the pore space in the dried brick required to produce plasticity. There is a relation between fineness of grain and percentage volume of shrinkage, but it is less well marked, and the relation to the tensile strength of the dried material is also clear but even less marked.

Measurements of the tensile strength of the dry material are particularly open to objection as a measure of plasticity, since the tensile strength must depend largely upon the amount of soluble cementing material, which in turn depends upon other factors than the fineness. It has been repeatedly observed that materials are plastic when ground wet which are nonplastic when ground dry. Probably in each case the plasticity is estimated on the basis of the tensile strength. We understand that the United States Office of Public Roads and Rural Engineering formerly tested materials for their binding power uniformly in both the wet and dry condition, and that it was a universal experience that wet grinding gave the greater binding power. It should not be overlooked that here chemical composition of the material is of importance.

No work seems to have been done on the flow of plastic substances through long tubes as a measure of plasticity. Some work has been done on the flow of such materials through orifices, which corresponds to the conditions necessary for hydraulic flow. The effort has been made to measure the so-called "viscosity" of plastic materials such as paint by means of paddle-wheel viscometers or instruments of that type. It is quite possible that measurements with this latter type of instrument have the highest significance, but it is manifest that instead of expressing the results in terms of "viscosity" they should be based on the application of the laws of plastic flow.

Among the experiments with orifices, Bleininger and Ross[27] have shown that the more plastic substances require the most water to render them plastic, but that all require about the same force of 50 pounds per square inch to start the flow. This seems to be equivalent to saying that in their most workable condition all clays should have about the same friction, but since for a given friction the most plastic clays will contain the most water, they will have the highest mobility and slippage.

Simonis[28] made some interesting experiments using 40 g of Zettlitz earth made up with 100 g of water and to which were added successive portions of a dilute solution of sodium hydroxide containing 1.795 g per liter. The pressures seem to have been measured in centimeters of water head and the volume of flow in the number of cubic centimeters which would flow in 600 seconds. He measured the flow of 16 mixtures and pure water, designated by the numbers given on the curves in Fig. 12. The amounts of sodium hydroxide added are given in the second column of Table 20.

---

[27] Trans. Amer. Ceram. Soc., 16, p. 392; 1914.

[28] Sprechsaal, 38, pp. 597, 881, 1625; 1905.

TABLE 20

Simonis's Experiments on the Flow of Suspensions of Zettlitz Earth through a 2-mm Orifice

No.	Ml NaOH sol.	Pressure																	
		15	16	17	18	20	22	25	30	35	40	45	50	60	70	80	90	100	110
1	0	Obs.													8.9	14.8	20	39	58
		Calc.													0	0	0	0	0
2	2	Obs.												4.1	13.3	26.6	45.2	104	234
		Calc.												0	0	0	0	0	0
3	4	Obs.			f =93.3									9	18	43	180	348	464
		Calc.			f′=98.0									0	0	0	0	221	455
4	5	Obs.			f =84.0								1.7	13.8	48.5	192	384	588	852
		Calc.			f′=83.9								0	0	0	74	308	542	779
5	6	Obs.			f =72.2						8.5		10.5	48	156	392	666	920	1176
		Calc.			f′=69.8						0		0	0	173	407	641	875	1110
6	7	Obs.			f =60.7								59	200	414	486	972		
		Calc.			f′=55.7								0	269	503	737	971		
7	8	Obs.			f =42.2				2	32	120	260	336	660	804	1068	1248		
		Calc.			f′=41.6				0	0	131	248	365	599	833	1067	1301		
8	9	Obs.				50	90		232	360	450		746	1020	1140			f =26.9	
		Calc.				0	0		227	344	461		695	929	1164			f′=27.5	
9	10	Obs.			284				588	648	792	960	1116	1212				f =13.3	
		Calc.			276				557	674	791	908	1025	1259				f′=13.4	
10	11		510		612	632		720	900	996	1044							f = 0.0	Obs.
			543		590	637		754	871	988	1094							f′= 0.0	Calc.
11	12		528	540	540	624		672	996									f = 0.0	Obs.
			543	566	590	637		754	871										Calc.
12	14	576		600		720			996									f = 0.0	Obs.
		520		566		637			871										Calc.
13	18		360	480		720			972									f = 0.0	Obs.
			543	566		637			871										Calc.

14	22	372	....	480	....	720	....	....	972	....	....	....	....	....	....	....	....	f = 0.0	Obs.
		520	....	566	....	637	....	....	871	....	....	....	....	....	....	....	....	....	Calc.
15	26	....	....	744	....	720	....	....	996	....	....	....	....	....	....	....	....	f = 0.0	Obs.
		....	....	566	....	637	....	....	871	....	....	....	....	....	....	....	....	....	Calc.
16	30	636	....	696	....	756	....	....	996	....	....	....	....	....	....	....	....	f = 0.0	Obs.
		520	....	566	....	637	....	....	871	....	....	....	....	....	....	....	....	....	Calc.
H_2O	528	....	....	....	....	618	....	....	996	....	....	....	....	....	....	....	....	f = 0.0	Obs.
		....	....	....	....	637	....	....	871	....	....	....	....	....	....	....	....	....	Calc.

The curves are nearly linear except when the volume of flow is small. The curvature is again probably due to seepage as in our own experiments. The horizontal distance of the different curves from the curve No. 10 is evidently a measure of the friction constant. The values of the friction constant f as obtained graphically are given in the table. We may calculate these values by means of the formula

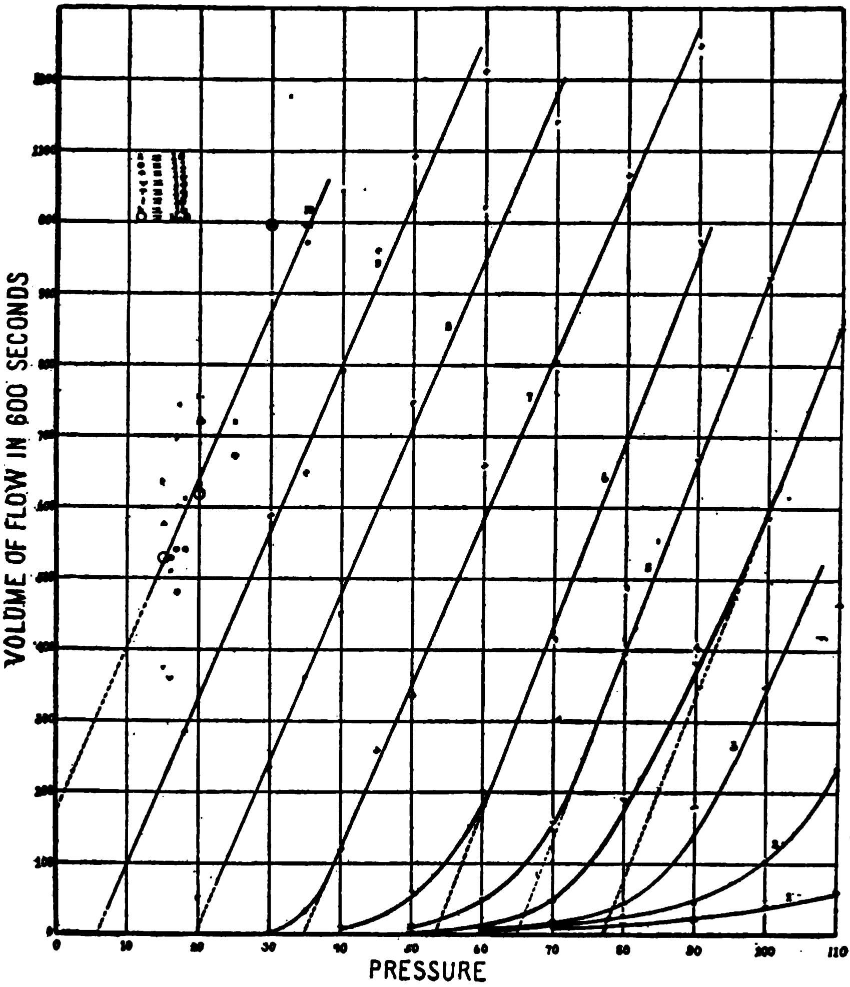


FIG. 12.—*Plastic flow from an orifice. Adapted from Simonis*

$$f' = 154 - 14.1\ c$$

where c represents the number of cubic centimeters of sodium hydroxide added. It appears, therefore, from a comparison of

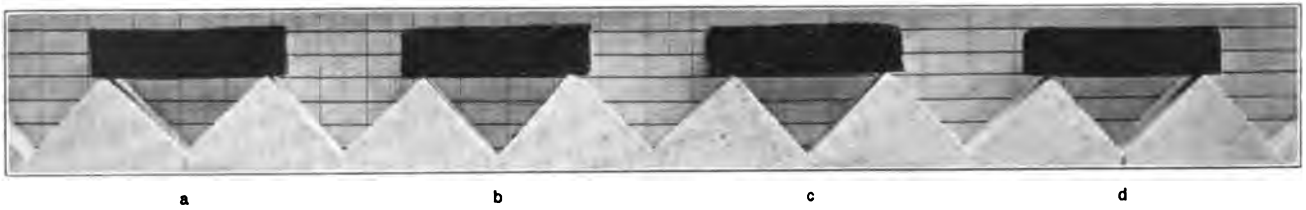


FIG. 13

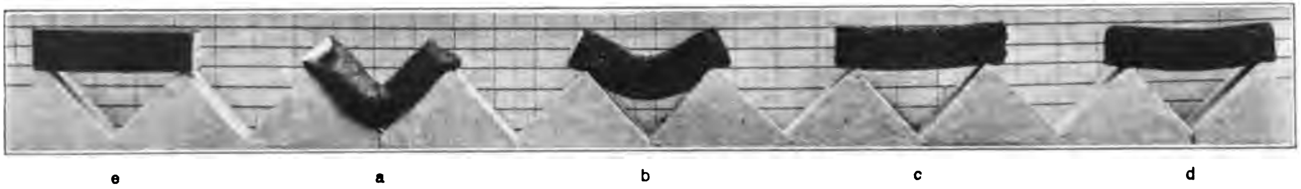


FIG. 14

the values of f and f' that Simonis's experiments confirm our conclusion from our own experiments that the friction is a linear function of the concentration. We note that the friction constant continually decreases as the water is added until 11 cm^3 have been added, after which further additions have no effect upon the rate of flow.

The fact that the curves are sensibly parallel constitutes a remarkable difference between his results and our own. The fact that his curves are parallel signifies that all of the plastic mixtures have the same mobility and that all of the viscous mixtures have the same fluidity, or what amounts to the same thing, the rate of flow is independent of the fluidity or mobility. This is characteristic of the flow through an orifice, where the rate of flow, as calculated from equation 1a or equation 15, is

$$\frac{V}{tk}=\pi r^2\sqrt{\frac{pg}{m\rho}},$$

since l is equal to zero. It appears, therefore, that Simonis's experiments are to be regarded as a study of the hydraulic flow of plastic materials.

We can calculate the higher rates of flow quite accurately by means of the formula

$$U=23.4\ (P-f')+168.7$$

as seen in Table 20. The agreement between the observed and calculated values decreases as the rate of flow is lowered.

VI. MODELS OF PLASTIC FLOW

It was thought that the views of the nature of plastic flow here presented might be more convincing if a working model could be constructed. Ottawa sand of specific gravity of 2.638 and 20 to 30 mesh was found to have a pore space of 34.5 per cent. Coal-tar pitch of specific gravity of 1.28 was added to two portions of the sand to the extent of 30 and 40 per cent by volume. These materials after being thoroughly mixed were made into briquettes 4 by 1 by 1 cm and laid on two supports 3.3 cm apart. In Figs. 13 and 14 a briquette of the pure pitch is shown at *a*, the second photograph being taken 28 days later than the first. It is evident that the pitch is a viscous liquid since it flows readily under the very small force here exerted by gravity. The material with 40 per cent pitch, (*b*), is only less fluid, being still viscous, as shown by the marked sagging. The material with 30 per cent pitch (*c*) is still less fluid, but it can hardly be called plastic since there is very perceptible sagging, and yet the pitch is considerably less than sufficient to fill the pore spaces completely, so that the material is lacking in strength. It may be said therefore that the coarse sand is nonplastic.

Some of the coarse sand was ground and passed through a 20-mesh sieve, and with this briquettes were made containing 40 and 45.5 per cent of pitch. We see in Fig. 14 (*d*) that with even as high as 45.5 per cent of pitch the fluidity is very slight. With 40 per cent (*e*) we have a truly plastic material since now after the elapse of several months the sagging is hardly perceptible. And it may be added that the material has very great strength.

VII. SUMMARY

1. The various types of viscous and plastic flow have been considered theoretically. According to the circumstances of the flow the viscosities may be additive, the fluidities may be additive, or slipping or seepage may enter in to affect the character of the flow. The possible separation of the components of a mixture by means of flow has been considered. It has been shown that in a suspension of solid particles in a liquid there must be a dissipation of energy when the solid particles collide, as they must collide if the layers of the suspension move over each other. This dissipation of energy follows the laws of ordinary friction and not the laws of viscosity.

2. Measurements have been made upon the flow of clay suspensions of different concentrations through capillaries of varying dimensions and at two temperatures.

3. It is shown that plastic flow can be sharply differentiated from viscous flow by the "friction" necessary to start plastic flow. The friction is a linear function of the volume concentration. It is also affected by the presence of alkalies or acids, but it is independent of the length or diameter of the capillary as well as the temperature of the medium.

4. For medium pressure the rate of efflux is given by the formula

$$v = K(P - f),$$

where P is the pressure, f is the friction, and K is an arbitrary constant. The experiments indicate that at low pressures seepage takes place causing a perceptible change in the concentration, and that at high pressures there is slipping which under certain circumstances may cause a sudden increase in the rate of flow.

5. The fluidity becomes zero at the concentration of solid where the plastic flow begins; that is, where the friction begins to have a positive value. This concentration, where the particles are able to form a bridge across the capillary space, is reached long before the concentration corresponds to close packing of the solid particles. For very fine-grained material the range between the concentration giving zero fluidity and the concentration corresponding to close packing will be much greater than in coarse-grained material.

6. The "mobility" of suspensions has been defined and calculated. The mobility decreases very rapidly from its maximum value in the concentration which has zero fluidity to a value not far from zero in the mixture which corresponds to close packing of the solid particles. The mobility increases with the fluidity of the medium, but it is also greatly affected by the presence of alkalies or acids.

WASHINGTON, March 2, 1916.

⁂

ج٢

DISTRIBUTION OF ENERGY IN THE VISIBLE SPECTRUM OF AN ACETYLENE FLAME*

By W. W. Coblentz, Associate Physicist, and W. B. Emerson, Laboratory Assistant

CONTENTS

Page
I. Introduction.......... 355
II. Experimental data.......... 357
  1. The acetylene flame.......... 357
  2. The spectroradiometers.......... 358
    Spectroradiometer No. 1.......... 358
    Spectroradiometer No. 2.......... 360
    Spectroradiometer No. 3.......... 360
III. Discussion of data.......... 363
IV. Summary.......... 363
V. Additional data.......... 364

I. INTRODUCTION

Data on the distribution of energy in the visible spectrum of a standard source of light are frequently needed by experimenters who are not in a position to determine for themselves the energy distribution. Frequent requests for such data have come to this Bureau and an attempt has been made to supply the desired information.

The acetylene flame appears to be a promising light source, having a high intensity and a white color. During the past six years the distribution of energy in the visible spectrum of this flame has been subjected to numerous investigations.

In a previous communication[1] data were published on the spectral energy distribution of a flat acetylene flame radiating edgewise into the slit of a mirror spectrometer, containing a fluorite prism and a vacuum bolometer. The energy distribution in the region of the spectrum from the blue to the extreme violet was obtained with a spectrometer containing plano-convex lenses and a quartz prism. The investigation showed that the energy distribution was a function of the thickness of the flame. This variation of emissivity with thickness of the flame was found to be very marked in the infra-red, and continued to be appreciable into the visible spectrum—at 0.68μ.

---

* Additional copies of this publication may be procured from the Superintendent of Documents, Washington, D. C., at 5 cents per copy.

[1] Coblentz, this Bulletin, 7, p. 243, 1911; reprinted in vol. 9, p. 109, 1912.

The demand arising for more precise data, the investigation was undertaken anew in 1913, using more sensitive radiation instruments, which permitted making more precise measurements in the blue and violet parts of the spectrum. It was then found that in the flat acetylene flame, observed flatwise and also edgewise, the variation in emissivity with thickness was even more marked throughout the spectrum than previously recorded. From this it appears that the distribution of energy in a flat acetylene flame can not be standardized. However, the cylindrical flame from a specified burner seemed to give sufficiently concordant results to warrant its use as a standard of light for investigations which do not require the highest attainable precision, in the spectral energy distribution.

Important optical work, employing light stimuli, is being done with spectrometers having collimating lenses of glass and of quartz. The question arose as to whether the energy distribution can be determined with an achromatic doublet, and especially with a plano-convex quartz lens, provided corrections are made for changes in aperture with change in wave length. The investigation of the plano-convex quartz lens for spectral energy distribution as compared with a mirror spectrometer (which is the recognized method for making spectral-energy measurements) was made about two and one-half years ago; but the data were not published.

Recently in connection with an investigation of the visibility of radiation, a wide aperture, achromatic doublet (computed by E. D. Tillyer) was subjected to test for spectral energy distribution. The data obtained are in complete agreement with those obtained with the mirror spectrometer, and also with the spectrometer having plano-convex quartz lenses. These data are not in agreement with those previously published[3] on the flat flame viewed edgewise. The former data are therefore withdrawn in view of the difficulty in using a flat flame, viewed edgewise, and in view of the apparently greater reliability of the present data on the cylindrical flame of the dimensions specified. In giving the new data it is to be emphasized that whenever possible the energy distribution of the acetylene flame used should be determined experimentally, at least in the red and yellow part of the spectrum, where the intensity is high (hence easy to observe) and is subject to variations (in the red) with thickness of the radiating layer of the flame. In the region of the spectrum extending from the yellow to the extreme violet the energy distribution of all acetylene flames, whether cylindrical or flat (examined flatwise and edgewise), was found to coincide, indicating that the radiation is sufficiently saturated so that the data given herewith may be considered applicable to the various acetylene burners commonly used.

---

[3] This Bulletin, 7, p. 243; 1911.

However, as already stated, in the region from the red toward the longer wave lengths the emissivity is greatly affected by change in thickness of the flame so that it is important to use a cylindrical flame of the dimensions specified in order to insure accuracy.

II. EXPERIMENTAL DATA

1. THE ACETYLENE FLAME

The data given in this paper pertain to a cylindrical acetylene flame, produced by a single-jet "Crescent *Aero*" burner,[3] consuming one-fourth cubic foot of gas per hour. The acetylene gas was made from commercial calcium carbide. It was produced by an automatic generator[4] and supplied to the burner under a water pressure of 7.5 cm (as measured at the outlet).

The automatic generating apparatus supplied the gas at a very uniform pressure, which is important in accurate work.

The height of the luminous part of the flame, as measured from the lava-tip burner, was about 3.5 cm and the thickness was about 3 mm. No doubt other makes of burners giving a flame of the dimensions herein specified will give similar results. In the recent investigation the flame was placed a short distance (about 15 mm) from the spectrometer slit, which was either 4 or 12 mm in height. In this manner the spectral energy distribution of a height of 4 mm and of 12 mm of the thickest part of the flame was obtained. (See Fig. 1.)

---

[3] Obtained from the Crescent Burner Manufacturing Co., New York.

[4] A "Pilot, Model D," acetylene generator made by the Acetylene Apparatus Mfg. Co., Chicago, Ill.

The acetylene flame has been employed in this Bureau in radiometric investigations extending over a number of years, and it has proven a very convenient and constant source of radiation. A photometric investigation of the acetylene flame as a source of light for standardizing photographic plates, made by Jones,[5] also shows a great constancy in the behavior of this (flame) source of radiation.

The acetylene flame is, of course, subject to agitation by air currents, but it is easily rendered steady by the simple device of having it situated at a distance of about 3 mm from a sheet of metal, which is perforated by a slit 2 mm wide and 6 to 12 mm high, depending of course upon the use to which the flame is to be put for illumination. Such a simple shield, shown in Fig. 2 *A*, has been used satisfactorily in the various investigations made in this Bureau during the past six years. In order to make a light-tight inclosure a shield has recently been provided which is of the form shown in Fig. 2 *B*. However, for steadying the flame the device does not appear to be any more efficient than a strip of sheet iron, about 15 cm long and 10 cm wide, bent into the form shown in Fig. 2 *A*.

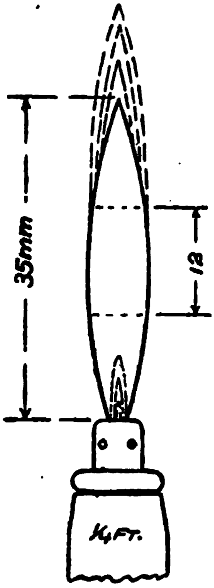


FIG. 1.—*Acetylene burner and flame*

2. THE SPECTRORADIOMETERS

The data presented in this paper are based upon the spectral energy distribution obtained with three different types of spectroscopes differing widely in dispersion and differing entirely in construction of the optical parts.

Spectroradiometer No. 1.—The spectroradiometer having the smallest dispersion and the highest intensity of radiation consisted of (1) a pair of plano-convex quartz lenses (cut perpendicular to the optic axis) 18 cm. in focal length and 6 cm. in diameter, (2) a 60° quartz prism, and (3) a radiometer consisting of a bismuth-silver thermopile and auxiliary galvanometer, both of which instruments have been described in previous communications in this Bulletin. In order to obtain a normal spectral energy curve from the data obtained with this outfit it is necessary to apply corrections (1) for reflections from the faces of the prism and the lenses (column 6, Table 1), (2) for change in slit width with change in focal length (column 5, Table 1), and (3) for change in energy intercepted with change in aperture with focal length. The latter correction is important because the factor enters as the square of the focal length. These data are given in column 7 of Table 1. The complete data for reducing the prismatic energy distribution to normal are given in column 8 of Table 1. They are to be considered supplementary to the optical constants of quartz previously published.[6] The distribution of energy in the spectrum, obtained from the observations when using this quartz spectrometer outfit, is given in Fig. 3. The data are in excellent agreement with those obtained with other spectroradiometers having a much larger dispersion. In the extreme violet the energy is probably a trifle high, due to the presence of diffuse light.

---

[5] Jones, Trans. Illum. Eng. Soc., 9, p. 716; 1914.

TABLE 1

Data for Reducing Prismatic Spectral Energy Curves to Normal when Using a Spectroradiometer Consisting of a 60° Quartz Prism and a Pair of Plano-Convex Quartz Lenses Having a Focal Length of 18 cm for $\lambda=0.5876\mu$

Spectrometer setting	Wave length	Focal length	Angular slit width for different focal lengths	Slit width corrected for change in f. l. = S.W.	Transmission; $\frac{(1-r_1)^6\times\{(1-R_1)^2+(1-R_2)^2\}}{2}=T$	$\left(\frac{1}{f_\lambda}+\frac{1}{f_{.587\mu}}\right)^2=\frac{1}{f_1^2}$	$SW\cdot\frac{1}{f_1^2}\cdot T$
° ′	μ	mm	′	μ			
−0 30	0.7828			0.0880	0.6678	0.9562	0.0562
K	.7665	184.0	9.79				
25	.7398			.0789	.6669	.9640	.0507
20	.7020			.0706	.6661	.9720	.0457
15	.6681			.0634	.6653	.9745	.0411
He	.6678	182.1	9.90				
10	.6383			.0570	.6646		.0372
− 05	.6119			.0513	.6637		.0338
0 00	.5876	180.0	10.00	.0464	.6629	1.000	.0308
+ 05	.5654			.0419	.6621		.0278
10	.5451			.0380	.6612		.0254
15	.5269			.0343	.6604		.0233
20	.5111			.0317	.6597		.0215
He	.5015	176.9	10.17			1.035	
30	.4830			.0270	.6581		.0186
40	.4591			.0233	.6565		.0162
He	.4472	173.8	10.34			1.074	
50	.4378			.0203	.6549		.0145
+1 00	.4193			.0180	.6533		.0130
10	.4029			.0161	.6516	1.115	.0117
He 20	.3889	170.0	10.65	.0144	.6500	1.121	.0106
30	.3764			.0131	.6485		.0099
40	.3652		10.85	.0120	.6471		.0091
50	.3550			.0111	.6455		.0085
+2 00	.3452			.0102	.6439	1.212	.0080

---

[6] This Bulletin, 11, p. 471; 1914.

Spectroradiometer No. 2.—The second outfit used in the energy measurements in the spectrum of the acetylene flame consisted of a spectrometer with (1) silvered-glass mirrors 50 cm. in focal length, (2) a perfectly clear, 60°, fluorite prism, and (3) a vacuum bolometer. This outfit has been described in a previous communication,[7] in which data are given for eliminating the absorption in the silver mirrors and for reducing the observations to a normal spectrum. In a mirror spectrometer the question of achromatism does not enter into the work, and the change in astigmatism is inappreciable. Owing to the larger dispersion which obtained in this spectroradiometric outfit (about twice that of spectroradiometer No. 1) and the small aperture of the prism, the energy measurements could not be extended into the extreme violet. The data are in excellent agreement (Fig. 3) with those obtained with the other spectroradiometers. As already mentioned, the investigation of the acetylene flame with these two instruments was for the purpose of testing the quartz-lens outfit as a spectroradiometer and for obtaining data on the acetylene spectrum in the extreme violet. The data pertaining to these two spectroradiometers were obtained some years ago, but never published.

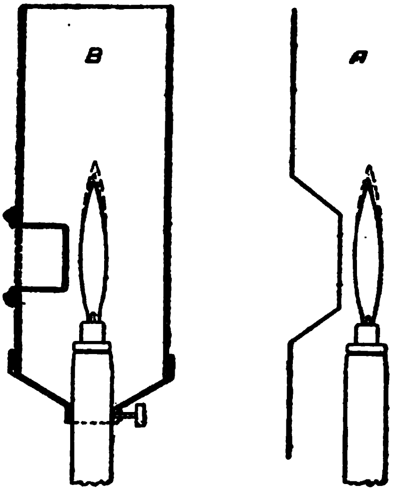


Fig. 2.—*Shields for an acetylene flame*

Spectroradiometer No. 3.—The data recently obtained relates to a spectroradiometer having (1) achromatic lenses (cemented doublets computed by E. D. Tillyer) 5 cm in diameter and 31 cm in local length, (2) a 60° prism of light flint glass, and (3) a bismuth-silver thermopile, in a monochromatic illuminator mounting.[8]

The calibration and slit-width curve of the prisms used in the two preceding spectroradiometers were obtained from the refractive indices. Not knowing the refractive indices of the flint-glass prism the scale of wave lengths was calibrated by noting the spectrometer circle readings for various helium lines, from a vacuum tube operated on a 2000-volt transformer. The spectrometer was provided with an automatic device for maintaining the prism at minimum deviation, the fiducial point being the yellow helium line $\lambda = 0.5876\mu$ and the spectrometer circle reading being

---

[7] This Bulletin, **10**, p. 1; 1913.

[8] This Bulletin, **11**, p. 154; 1914.

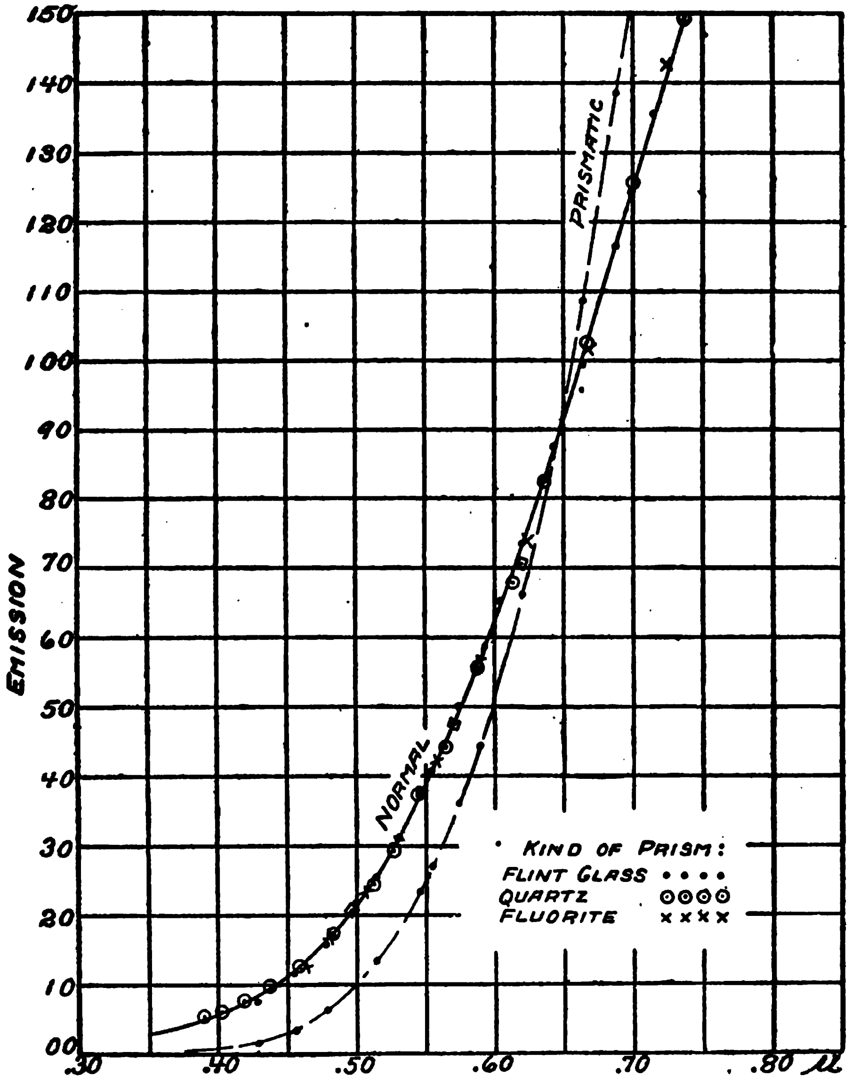


FIG. 3.—*Energy distribution in the visible spectrum of a cylindrical acetylene flame as observed with three types of spectroradiometers*

310° 00′ 00″, as shown in Fig. 4. This illustration gives the calibration curve and the curve of slit widths for reducing the prismatic energy measurements to the normal spectrum. For the information of those who are not thoroughly familiar with the subject, it may be added that the slit widths were obtained by noting the wave lengths for any two spectrometer settings which are 10 minutes apart. The difference in wave lengths of these two settings is the slit width (in wave lengths) at the mid-point of these two spectrometer circle readings.

The flint-glass prism and the 31 cm focal-length lens produced a dispersion which is about four times that of the quartz outfit in spectroradiometer No. 1, the actual length of the spectrum being

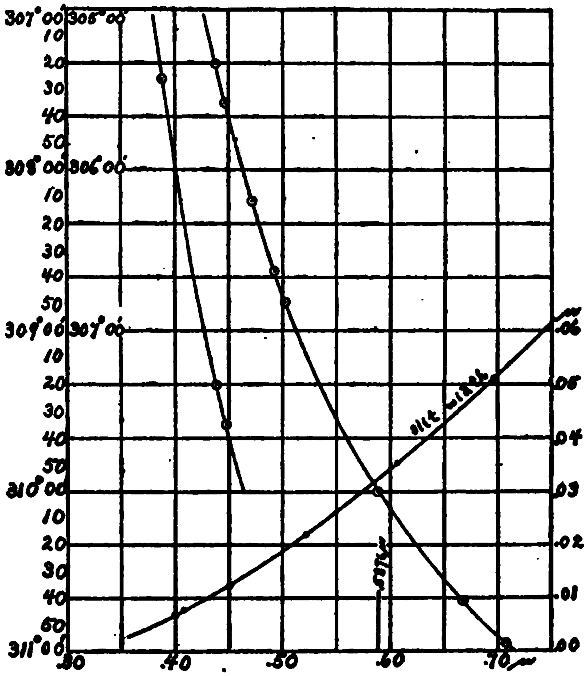


FIG. 4.—*Calibrations and slit-width correction curves of a flint-glass prism, B. S. 2425 B*

about 14 mm between the red and the blue-violet helium lines ($\lambda = 0.667\mu$ to $\lambda = 0.447\mu$). However, the wide aperture of the lenses (and prism) produced sufficient intensity so that it was possible to extend the observations into the violet, where the absorption of the prism becomes apparent, as shown in Fig. 3. Throughout the spectrum the data obtained with this apparatus are in excellent agreement with those obtained with the two preceding spectroradiometers. The slits used were, respectively, 4 and 12 mm in height, as already mentioned, and the energy curves of the acetylene flame were found in coincidence throughout the whole region to $\lambda = 0.75\mu$ when they were in coincidence to 1 part in 180.

In view of the difficulties experienced in radiometric work it may be added that such investigations are best made in the summer (between May and September), when there is only a small difference of temperature within and without the laboratory. In this manner one can make galvanometer readings to 0.1 mm in July that can not be read closer than 0.3 to 0.5 mm in midwinter.

III. DISCUSSION OF DATA

The observations on the energy distribution of a cylindrical acetylene flame made with three different types of spectroradiometers are shown graphically in Fig. 3. They are in excellent agreement throughout the spectrum. The data read from the curve drawn through these observations are given in Table 2.

As mentioned on a preceding page, the present data supersede those published some years ago in view of the greater certainty in the reproducibility of conditions which obtain in a cylindrical flame as compared with a flat flame, to which the previously published data apply, when that flame was used edgewise.

TABLE 2

Spectral Energy Distribution of an Acetylene Flame

[Mean of 3 sets for cylindrical flame; (1) quartz prism and plane-convex quartz lenses; (2) fluorite prism, mirror spectrometer; (3) Light flint glass prism, achromatic glass lenses]

λ	E (normal)	λ	E (normal)	λ	E (normal)	
μ		μ		μ		Bray tip
350	3.1	480	17.0	625	75.7	....
360	3.3	500	21.9	640	84.7	....
375	4.0	520	27.9	650	91.1	....
380	4.4	525	29.5	660	97.4	....
400	5.9	540	35.0	675	107.5	....
420	7.7	550	38.9	680	110.9	....
425	8.2	560	42.9	700	124.6	125.8
440	10.0	575	49.8	720	138.5	140.7
450	11.4	580	52.2	725	141.9	144.5
460	13.0	600	62.1	740	152.0	155.8
475	16.0	620	73.0	750	158.9	163.7

IV. SUMMARY

This paper gives numerical data on the distribution of energy in the visible spectrum of a cylindrical acetylene flame from a certain type of burner and operated under certain conditions. In the region of the spectrum extending from the yellow to the violet the spectral energy distribution of all the flames examined appears to be the same, within the limits of observation. On the other hand, in the region of the spectrum extending from the red toward the long wave lengths, the emissivity is greatly affected by variation in thickness of the radiating layer of incandescent particles in the flame. Hence, in and beyond the red part of the spectrum the data apply only to cylindrical flames which are operated under specified conditions.

V. ADDITIONAL DATA

Since the completion of the measurements just described an opportunity was presented to determine the distribution of energy in the visible spectrum of the "Bray" tip[9] (¼-foot capacity) used by Dr. Nutting in his researches on the visibility of radiation.[10] This burner gives a cylindrical flame which is about 5 cm high and slightly greater in diameter than the one just described. This lamp has been thoroughly investigated[11] as a standard of light, giving a high intensity; and it appears to be very reliable in operation.[12] This flame may be more useful than the one just described in view of its larger dimensions. This permits operating it under various pressures without seriously affecting the energy distribution.

The light from this flame is emitted through an opening 3 mm in height. For certain radiometric work it would be better to use an opening 4 to 5 mm in height.

The distribution of energy in the visible spectrum was determined with spectroradiometer No. 3, when the flame was operated on its normal (90 mm) water pressure; also on a water pressure of .73 mm. The two energy curves coincided within the limits of experimental error, showing that, although the candlepower had changed, the color had not changed very markedly. There was a slight indication of a higher emission at 0.75 μ (redder flame) when operated on a pressure of 73 mm; but it amounted to only about 1 per cent.

The distribution of energy in the flame, from the "Bray" and the "Crescent *Aero*" burners, is the same throughout the visible spectrum to 0.70 μ, where the former begins to increase in emissivity, as given in the last column of Table 2.

WASHINGTON, January 18, 1916.

---

[9] Thorn and Hoddle Acetylene Co., London, England; Crane, New York.

[10] Nutting, Trans. Illum. Eng. Soc., 9, p. 633; 1914.

[11] Jones, Trans. Illum. Eng. Soc., 9, p. 716; 1914.

[12] Copies may be obtained from the Research Laboratory, Eastman Kodak Co., Rochester, N. Y.

FURTHER EXPERIMENTS ON THE VOLATILIZATION OF PLATINUM

G. K. Burgess, Physicist, and R. G. Waltenberg, Assistant Physicist

The experiments here described are an extension of those of Burgess and Sale,[1] undertaken at the suggestion of Dr. W. F. Hillebrand, chairman of the committee on quality of platinum utensils of the American Chemical Society. In the earlier papers are described a convenient thermoelectric method of testing platinum purity and observations on loss of weight of crucibles subjected to heating at 1200° C and subsequent acid treatment, together with certain magnetic and photomicrographic observations.

The present investigation consists of a series of observations on change in weight of several platinum crucibles of various degrees of purity when subjected to heating at 700°, 1000°, and 1200° C. Determination of the loss of iron content after successive heatings and of other materials soluble in hydrochloric acid have also been made, as well as a few observations by treatment with hydrofluoric acid to detect the presence of silica, which may come largely if not entirely from the marquardt porcelain portions of the furnace described in previous papers, to which papers reference should also be made for the details of apparatus and methods.

The choice of heating temperatures of 700°, 1000°, and 1200° C proved a fortunate one, in that it not only covers the temperature range to which platinum crucibles are ordinarily subjected in practice, but besides it so happens that there also occurs within this temperature interval a reversal from a loss to a gain in weight of all grades of platinum ware observed in this investigation.

---

[1] J. of Ind. and Eng. Chemistry, 6, p. 452, 1914; 7, p. 561, 1915; Scientific Paper No. 254, this Bureau, 1915.

The observations and the numerical inferences from them are recorded in Tables 1 and 2 for the seven crucibles of this investigation, ranging from the purest thermoelement and "tiegel platin" ware of Heraeus to crucibles containing up to 2.7 per cent iridium and 8 per cent rhodium and with divers amounts of iron and other unknown soluble materials (including probably Pt itself, which in presence of Fe is slightly soluble in HCl) also as impurity. Five of these crucibles—all except I and II, which are practically new—had been used in the previous investigation at 1200° C.

The crucibles which had been previously heated at 1200° C were heated at 1000° C and then at 700° C; the others were heated in the reverse order: 700°, 1000°, and 1200° C. When crucibles have been prepared for use by strong ignition and treatment with acid there is apparently no difference in the loss in weight due to reversing the order of heating. This would be expected from the previous work at this Bureau. The experimental operations were, in brief, as follows:

Before heating, each crucible was cleaned and weighed. The furnace was brought to the temperature desired, then the crucible was placed in it and allowed to remain for four hours. (In the work of Burgess and Sale at 1200° C the crucibles were heated for two-hour periods.) The crucibles were then taken out of the furnace, cooled in a desiccator, and weighed. A treatment for five minutes with boiling hydrochloric acid (1 acid to 4 water) followed. They were again weighed after washing followed by a slight ignition over a Bunsen burner. The iron in the hydrochloric acid solution was weighed as ferric oxide after precipitating with ammonium hydroxide; slight discrepancies appear in some of the results due to the ash uncertainty on ignition of the filter paper. The crucibles were usually heated three times at each temperature with similar treatment after each heating.

Table 1 shows the results of each treatment in milligrams per 100 cm^2 of platinum surface. Crucibles *b* and *n* are alloys containing about 0.19 and 7.95 per cent rhodium, respectively; the others contain iridium; *n* was made up specially and *b* is presumed from its behavior to contain rhodium.

For several crucibles the first treatment results in a loss appreciably greater than the succeeding ones. This illustrates the necessity of proper preparation of the crucibles before using for accurate determinations.

TABLE 1

Observations on Platinum Crucibles

Source or maker	Crucible reference	Weight (grams)	Volume (cm ^{3})	Area of surface (cm ^{2})	Emf (mv)	Iridium (per cent)	Rhodium (per cent)	Four hours at 700° C (loss in mg/100 cm ^{2})			Four hours at 1000° C (loss in mg/100 cm ^{2})			Four hours at 1200° C (loss in mg/100 cm ^{2})		
								Heat	Acid	Fe_2O_3	Heat	Acid	Fe_2O_3	Heat	Acid	Fe_2O_3
Heraeus, normal thermo-element Pt	a	17.2	27	77	0.1	0.05	....	+0.03	0.03	0.05	0.38	0.05	0.08	4.36	0.10	0.29
								+ .01	.06	.09	.23	.01	.00	1.68	.60	.43
								+ .01	.08	.05	.31	.04	.06	3.70	.12	.21
Heraeus, Tiegel platin....	I	18.0	26	82	2.6	.8	....	+ .00	.10	.11	1.06	.27	.18	....	....	....
								+ .07	.13	.07	.88	.24	.21	....	....	....
								.05	.16	.02	.51	.09	.00	....	....	....
Johnson Matthey Co., best crucible ware	b	26.2	33	106	.5	....	0.2	+ .02	.23	.08	.29	.20	.04	3.96	.48	.25
								+ .02	.16	.05	.35	.03	.02	1.92	.70	.40
								+ .08	.17	.06	.33	.10	.07	4.08	.30	.20
Baker & Co., commercial ware	k	23.9	34	79	6.5	2.4	....	+ .10	.65	.46	3.64	.25	.18	12.48	2.28	....
								+ .09	.48	.28	1.46	.15	.10	10.90	.78	....
								+ .03	.23	.18	1.50	.29	.09	5.88	2.02	....
Do..................	l	39.6	56	108	6.9	2.7	....	+ .08	.20	.14	.59	.52	.09	4.32	10.66	....
								+ .06	.17	.08	1.02	.21	.13	4.64	4.94	....
								+ .05	.15	.10	.80	.22	.19	10.16	5.58	....
Baker & Co., special Rh ware	n	19.9	24	79	9.7	....	8.0	+ .11	.10	.09	.56	.04	.05	1.22	.04	.18
								+ .13	.10	....	.10	.08	.01	2.88	.26	.34
								+ .10	.09	.08	.16	.07	.14	2.42	.08	.00
Quenessen, De Belmont, Legendre et Cie	II	15.4	22	78	2.7	.9	....	.07	.14	.13	2.47	.55	.45	4.02	.45	.38
								.27	.15	.10	1.01	.60	.46	3.98	.14	.43
								.00	.33	.15	1.00	.49	.21	....	....	....

Table 2 gives a summary of the results. The change in weight on heating at 700° C was very small, and in most cases was an increase (0.005 to 0.028 mg/100 cm^2/hour), but the loss with acid treatment was greater than the gain on heating in all but one case. The 8 per cent rhodium alloy, crucible *n*, gained a little more weight on heating than it lost with acid. This is due possibly to a small amount of silica deposited on the crucible from the furnace tube. On treating these crucibles with strong hydrofluoric acid, after the hydrochloric acid treatment, there was a loss, which for crucible *n* amounted to 0.24 mg/100 cm^2. There was no additional loss on repeating the treatment with hydrofluoric acid.

TABLE 2

Summary of Heating and Acid Tests

	Crucible, a; emf against Pt, 0.1 mv; equivalent alloy, 0.05 per cent Ir. Temperature of heating, °C			Crucible, b; emf against Pt, 0.5 mv; equivalent alloy, 0.2 per cent Rh. Temperature of heating, °C			Crucible, I; emf against Pt, 2.6 mv; equivalent alloy, 0.8 per cent Ir. Temperature of heating, °C			Crucible, II; emf against Pt, 2.7 mv; equivalent alloy, 0.9 per cent Ir. Temperature of heating, °C			Crucible, k; emf against Pt, 6.5 mv; equivalent alloy, 2.4 per cent Ir. Temperature of heating, °C			Crucible, l; emf against Pt, 6.9 mv; equivalent alloy, 2.7 per cent Ir. Temperature of heating, °C			Crucible, n; emf against Pt, 9.7 mv; equivalent alloy, 8.0 per cent Rh. Temperature of heating, °C		
	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200	700	1000	1200
Heat treatment loss, mg/100 cm²/hr..	+0.004	0.077	0.812	+0.010	0.081	0.830	+0.002	0.204	......	0.028	0.374	1.001	+0.018	0.550	2.438	+0.016	0.201	1.593	+0.028	0.069	0.543
Acid treatment loss, mg/100 cm²/hr...	.014	.008	.068	.047	.023	.123	.033	.050	......	.052	.137	.074	.113	.058	.423	.043	.079	1.765	.024	.016	032
Iron recovered as Fe_2O_3, mg/100 cm²/hr.	.016	.012	.078	.016	.011	.072	.017	.033	......	.032	.093	.100	.077	.031	......	.027	.034	......	.020	.017	.044
Total loss, heat+acid, mg/100 cm²/hr..	.010	.085	.880	.037	.104	.953	.031	.254	......	.080	.511	1.075	.095	.608	2.861	.027	.280	3.358	+ .004	.085	.575
Iron compared to total loss, per cent..	160	14	9	43	11	8	55	13	......	40	18	9	81	5	......	100	12	......	......	20	8
Iron compared to acid loss, per cent..	114	150	115	34	48	59	52	66	......	62	68	135	68	53	......	63	43	......	83	106	137
Acid compared to total loss, per cent..	140	9	7	127	22	13	106	20	......	65	26	6	119	10	15	159	28	52	......	19	6

The curves showing the relation between loss at 1200° C and the emf against pure platinum at 1100° C, including observations of Burgess and Sale, are reproduced in Fig. 1 and similar diagrams could be constructed for 700° and 1000° C. The loss on heating plus the loss with acid treatment is termed "total loss," and it is also shown in the plot for several crucibles. It is evident that crucibles containing iron lose less on heating than those which contain no iron, but their loss after the acid treatment is correspondingly greater. On some crucibles a surface film of iron oxide may be detected after heating, and the decreased loss on heating and increased loss with acid treatment is probably due to this iron oxide, as previously explained.

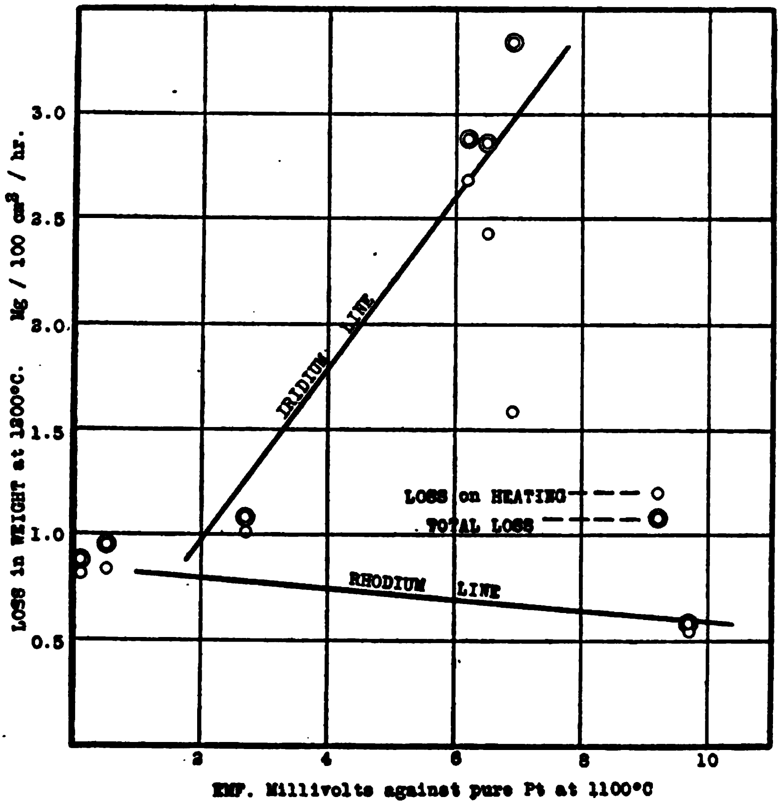


FIG. 1.—*Heating losses for crucibles containing Ir or Rh in terms of emf against pure Pt*

The relation between temperature and loss on heating for several crucibles is shown in Fig. 2. These curves are typical of certain classes of laboratory ware, i. e., pure platinum, platinum containing rhodium, and platinum containing iridium.

The loss in weight of platinum laboratory ware is here shown to be negligible below 900° C, but for all crucibles tested the loss at 1000° C is appreciable and rapidly increases with temperature.

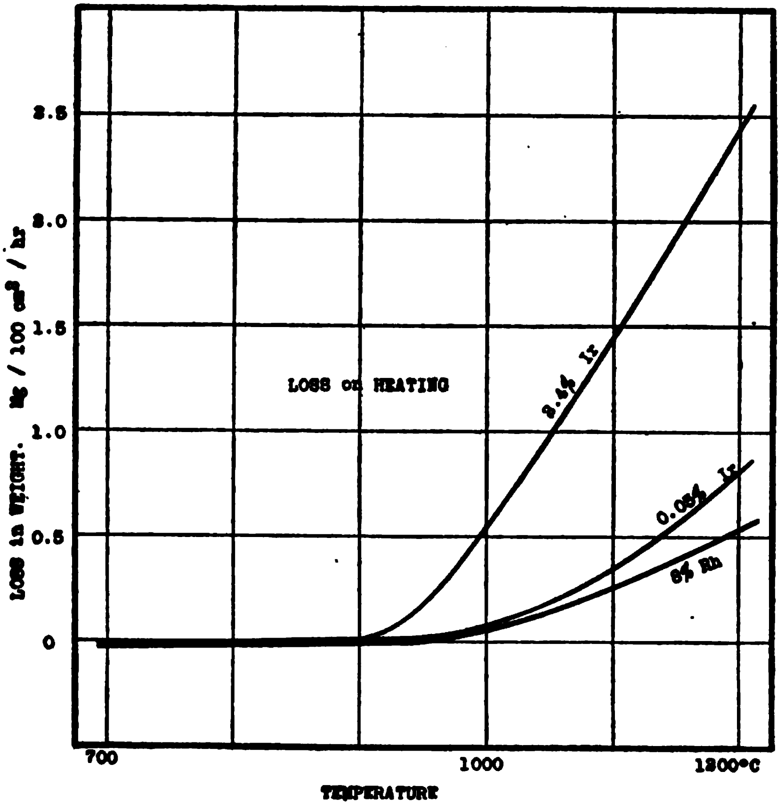


FIG. 2.—*Loss of weight, on heating crucibles containing rhodium or iridium, in terms of temperature*

The presence of rhodium, iridium, and iron in platinum produces similar results on heating at 1000 and at 1200° C. Rhodium decreases and iridium increases the loss of weight. Iron is objectionable because of the surface film of oxide which forms on heating the platinum containing it.

It is possible to predict the loss in weight of an iridium or rhodium alloy crucible on heating below 1200° C, provided the ware contains little iron.

In Table 3 are given the approximate changes in weight to be expected in mg/100 cm² of surface and per hour of heating of platinum nearly free from iron. The presence of iron in appreciable quantities renders the prediction uncertain, but it always acts in the direction of lowering the volatilization loss; silica, if taken up from the furnace, will also tend to lower the results slightly.

TABLE 3

Approximate Loss in Weight, mg/100 cm²/hour, at Temperatures Indicated for Platinum Nearly Free from Iron

Platinum containing—	Pure Pt	1 per cent Ir	2.5 per cent Ir	8 per cent Rh
900° C or less	0	0	0	0
1000° C	0.08	0.30	0.57	0.07
1200° C	.81	1.2	2.5	.54

Other metals, such as osmium, alloyed with platinum, may further decrease the loss on heating, and it is hoped to try some of them in the near future.

It was hoped to be possible, in this investigation, to carry out experiments with platinum crucibles alloyed with small quantities of osmium, but this was found to be impossible on account of the condition of the platinum market.

Experiments by other observers have recently been made which contribute data to this problem of the loss or gain in weight of heated platinum ware. Thus Vinal and Bovard [2] find on heating to about 600° C platinum voltameter dishes of 38 and 80 g. weight, freed from silver "very little change if any in the weight of the empty cups due to heating them to redness."

Sosman and Hostetter [3], investigating the reduction of iron oxides by platinum show, as would be expected from a consideration of the phase relations, that "if the existing pressure of oxygen is less than this equilibrium pressure, the oxide will dissociate and metallic iron will be absorbed by the platinum. If the pressure of oxygen be greater, on the other hand, iron from the platinum solution will be oxidized, the oxide will separate on the surface of the metal, and the concentration of the iron in the platinum will be reduced." In the experiments listed in the above tables we are of course working at a pressure high enough and at temperatures low enough for the second operation—oxidation of the iron.

---

[2] Scientific Paper No. 271, this Bureau; 1916.

[3] J. Wash. Acad., 5, p. 293; 1915.

SUMMARY AND CONCLUSIONS

In addition to the conclusions from the previous work of Burgess and Sale (loc. cit.), there may be noted the following:

1. Platinum ware in the form of crucibles of whatever degree of purity behaves, with respect to gain or loss of weight, on heating in air at ordinary atmospheric pressure in a manner characteristic only of the temperature of heating.

2. Each impurity as iridium, rhodium, or iron appears to exert its effect on the volatilization of platinum independently.

3. For platinum crucibles of all degrees of purity containing Ir, Rh, Fe, Si (up to a content of at least 3.0 per cent Ir) the loss on heating is negligible below about 900° C.

4. Below this temperature there may even be a slight gain in weight on heating platinum, owing to the iron content diffusing to the surface and oxidizing. At higher temperatures the presence of iron will lower the volatilization loss by amounts depending on the quantity of iron present. There appears to be no platinum made which does not contain some iron.

5. The volatilization of platinum containing rhodium is less than that of pure platinum at all temperatures above 900° C.

6. The volatilization of platinum containing iridium is, above 900° C, very much greater than that of pure platinum, and increases with the Ir content and with temperature.

7. It appears to make no material difference in the volatilization results, in the range 700° to 1200° C, what is the order of heating, ascending or descending temperatures.

8. In an oxidizing atmosphere at temperatures of the order of 1000° C. platinum, in the presence of, but not in contact with silica, will apparently take up small quantities of this substance.

9. The loss in crucible weight due to the solution of soluble matter in HCl, after heating, is variable, depending on the crucible, and may be large. This loss is relatively greater at low than at high temperatures.

10. All of the above losses, caused by heating, acid treatment, and iron diffusion, apparently continue with undiminished magnitude after the first treatment, which is usually erratic; although, eventually of course, the concentration of iron, etc., must become appreciably diminished.

WASHINGTON, April 13, 1916.

A STUDY OF THE INDUCTANCE OF FOUR-TERMINAL RESISTANCE STANDARDS

By Francis B. Silsbee

CONTENTS

Page.
I. Introduction 375
II. Historical 376
III. Definitions 377
IV. Relative methods 382
  1. Current-transformer method 382
  2. Mutual-inductance method 389
V. Absolute methods 390
  1. Computation 391
    (*a*) Parallel-wire type 392
    (*b*) Flat-strip type 393
    (*c*) Tubular type 397
  2. Quarter-phase method 402
  3. Change-of-resistance method 403
  4. Heating method 405
VI. Adjustment of final values 406
VII. Effect of stray fields 408
VIII. Observations on various types of shunt 409
IX. Notes on design 411
X. Mutual inductances 414
XI. Summary 421
XII. Notation 422

I. INTRODUCTION

Potentiometer and bridge methods are coming more and more into use in precise alternating-current measurements, and have created a demand for resistances and mutual inductances of known phase angle. This is particularly true of the present precise methods of testing instrument transformers.[1]

The residual inductance of resistance coils has been pretty thoroughly studied[2] in the range from 1 ohm to 10 000 ohms, but comparatively little work has been done above and below this range.

---

[1] As an example of the engineering importance of this work, consider a direct measurement of the power consumed in one of the current limiting reactances used by the New York Edison Co. The 2000-ampere current transformer needed would require the use of a 0.0001-ohm resistance standard for its calibration. An error as small as 1×10^{-9} henry in the assumed inductance of this standard would introduce an error of 33 per cent into the power measurement.

[2] Grover and Curtis, this Bulletin, 8, pp. 455, 495 (Reprints No. 175 and No. 177); Wagner, Elektrotech. Zs. **34**, p. 613, 1913; **36**, pp. 606, 621, 1915.

The object of the work described below was to study the range below 1 ohm. In this range standard resistances are almost invariably of the four-terminal type, and therefore require methods of measurement quite distinct from those applicable to the higher resistances. It was soon evident that the methods of comparing the time constants of two four-terminal resistances were much simpler and more accurate than the determination of the absolute value of any one. The work, therefore, naturally divides itself into two parts—first, the development of a method of comparison, and, second, a study of the various methods for the absolute measurement or computation of the inductance. The latter work has resulted in the establishment at the Bureau of Standards of a series of low resistances whose time constants are known to 0.1 or 0.2 microsecond.

Some of the methods used involved the use of mutual inductances of heavy-current capacity, and considerable time was spent in a study of the phase relations in such apparatus.

II. HISTORICAL

In 1906 E. and W. H. Wilson[3] published an account of some measurements on the inductance of shunts using an electrometer method. Since then, however, the subject has been confined to the standardizing laboratories where the need of precise values was first felt. At the National Physical Laboratory in 1909 Paterson and Rayner[4] constructed a series of shunts for use with alternating currents. Using manganin tubes cooled by a vigorous circulation of water they were able to obtain 2.5 volts drop in shunts as low as 0.001 ohm. They kept the time constant of their shunts small by the device suggested by Campbell[5] of using as potential lead a thin copper sheath just outside the working material. They computed the inductance directly from formulæ given by Russell[6] and did not attempt a direct measurement.

A few months later Orlich[7] published a description of the standards in use at the Reichsanstalt. These are of the flat-strip type. The inductances were measured by an electrometer method at 1935 cycles per second. Since this method gave only relative values of the time constants, Orlich constructed as standards two wire rectangles having inductances of about 2 microhenrys each. The measurements on the shunts of lower resistance were made by stepping down through the series.

---

[3] Electrician, **56**, p. 464; 1906.

[4] Inst. Elect. Eng. Journal, **42**, p. 455; 1909.

[5] Electrician, **61**, p. 1000; 1908.

[6] Russell, Alt. Currents, **1**, p. 53.

[7] Zeit. für Instrumentenkunde, **29**, p. 241; 1909.

At the Bureau of Standards Agnew and Fitch[8] used a dynamometer method analogous electromagnetically to the electrostatic method of Orlich and Wilson. They compared their working shunts with two standards, the inductance of which could be computed from the dimensions.

Sharp and Crawford[9] in 1910 published a description of a series of noninductive shunts constructed along the lines suggested by Drysdale. They were calibrated by stepping down from 0.1 ohm resistances which were assumed noninductive. The relative measurements were made by a Thomson double bridge, using a dynamometer excited in quadrature with the current in the resistance, as a detector.

III. DEFINITIONS

Standard resistances of less than 1 ohm are usually constructed with four terminals, to which leads may be attached. Two of these (the current terminals) are of comparatively massive construction and are intended to carry the current to be measured, while the other pair (the potential terminals) are smaller and are intended to be connected to some apparatus for measuring difference of potential. This form of construction is used for direct-current measurements because the value of the resistance is thereby made more independent of the manner in which the current leads are attached and because contact resistance is eliminated.[10] For alternating-current work this construction has the further advantage that the inductance of the apparatus which would otherwise be extremely variable is thereby made much more definite.

The various factors affecting the inductance of a four-terminal resistance standard (or as we shall for brevity call it "shunt") may be seen from a consideration of Fig. 1. If a sinusoidal alternating current I be passed through a piece of resistance material as $a\ b$, there will be a certain voltage between points a and b. This voltage will not, in general, be in phase with the current, but may be resolved into an in-phase and a quadrature component. The ratio of the in-phase component of voltage to the current may be taken as a definition of the resistance, and the ratio of the quadrature component of voltage to the current, as the reactance of the piece *a b*. The inductance is, of course, the reactance divided by 2 π times the frequency. This inductance may be denoted by L_{ab}.

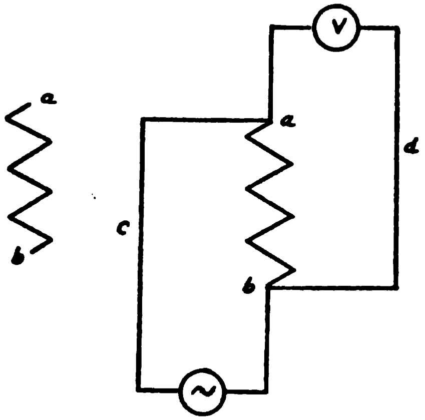
---

[8] This Bulletin, **6**, p. 281; 1909 (Reprint No. 130).

[9] A. I. E. E. Trans., **29**, p. 1537; 1910.

[10] For some general relations among four-terminal resistances see Wenner, this Bulletin, **8**, p. 559 (Reprint No. 181), 1912; Searle, Electrician, **66**, pp. 999, 1029; **67**, pp. 12, 54, 1911.

Now, in order that the current may flow through *a b*, the shunt must form part of a closed circuit containing a source of power, and the rest of the circuit will have a certain inductive effect on the voltage between *a* and *b*. Denoting the mutual inductance between the rest of the circuit and the part *a b* by $M_{ac,\ ab}$ we see that the resultant quadrature voltage between *a* and *b* will not be



(a) (b)

Fig. 1

$I\omega\ L_{ab}$, but $I\omega\ (L_{ab} \pm M_{ac,\ ab})$. The quantity $(L_{ab} \pm M_{ac,\ ab})$ may be called the "inductance of *a b* with return at *a c*," and denoted by $L_{ab,\ ac}$.

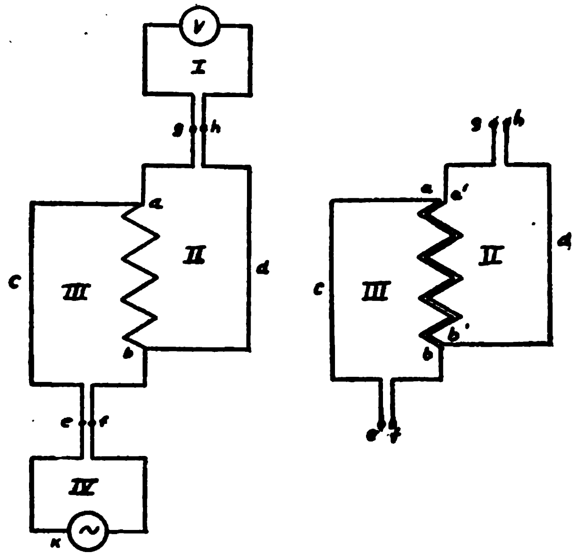
Furthermore, in order that the voltage between *a* and *b* may be measured, a second closed circuit must be formed as *abd* containing some arrangement for measuring voltage as *V*. Now there may be mutual inductance between the potential leads, such as *b d*, and the various parts of the current circuit. Let us denote these by $M_{ab,\ bd}$ and $M_{ac,\ bd}$. The quadrature component of the voltage as measured by *V* will then be not

$$I\omega\ L_{ab,\ ac}, \text{ but } I\omega\ (L_{ab,\ ac} \pm M_{ab,\ bd} \pm M_{ac,\ bd})$$

or in more detailed form

$$I\omega\ (L_{ab} \pm M_{ac,\ ab} \pm M_{ab,\ bd} \pm M_{ac,\ bd})$$

This quantity depends, in general, on the entire measuring circuit. It is desirable in practice to be able to consider the behavior of the shunt itself as distinct from the rest of the circuit. If the circuits are arranged as in Fig. 2 (*a*), we see that the two main circuits *acekfb*, and *abdhvg* may each be split up into two circuits each of which is nearly closed. The circuits *I* and *IV* are external to the shunt and any mutual inductance between *I* and *III* or *II* and *IV* may be made very small by proper arrangement of the apparatus and, in any event, may be classed as due to "stray fields" and not as part of the behavior of the shunt. This is also the case with the direct effect of *IV* upon *I*.



(a) (b)

FIG. 2

The points *gh* and *ef*, where the division into internal and external circuits occurs, are the terminals of the apparatus. We therefore get as the expression for the inductance of the shunt, the ratio of the quadrature component of the voltage between *g* and *h* to ω times the current flowing between *e* and *f*. This is the same as

$$L = L_{ab} \pm M_{ac,\,ab} \pm M_{ab,\,bd} \pm M_{ac,\,bd} \qquad (1)$$

where the *M*'s must now be considered as including only the mutual effects of circuits inside the terminals. In case the members of each pair of terminals are not close together, the position of the leads attached to them must be specified or the inductance will be indefinite. It is, of course, desirable to have the potential terminals as far away as possible from the current terminals, as the liability to error from stray fields is thus reduced.

It is useful in this connection to note that shunts may be divided into two main classes. In type I the working material itself is formed into a closed circuit. With this construction the current leads and the potential leads may be kept close together, and, if so, all the M's of equation (1) vanish and the inductance becomes that of a closed circuit and is, therefore, always positive. In type II the working material does not form a closed circuit and the inductance may be either positive or negative.

Instead of approaching the problem piecemeal, as was done above, we may consider two circuits *II* and *III*, as shown in Fig. 2 (*b*). The quadrature component of the voltage measured by V is $I \omega M_{\mathrm{II,III}}$, where I is the current flowing in circuit *II* and $M_{\mathrm{II,III}}$ is the mutual inductance of the two circuits. This quantity $M_{\mathrm{II,III}}$ may be split up into its parts as follows:

$$M_{\mathrm{II,III}} = M_{\mathrm{ab,a'b'}} \pm M_{\mathrm{ab,b'd}} \pm M_{\mathrm{ac,a'b'}} \pm M_{\mathrm{ac,b'd}}$$

If we now imagine the portion $a'b'$ to approach ab and finally coincide with it, we see that $M_{\mathrm{ab,b'd'}}$ approaches $M_{\mathrm{ab,bd}}$ and similarly for the other terms. Also $M_{\mathrm{ab,a'b'}}$ approaches L_{ab} since they are each defined as the ratio of the same voltage to the same current (divided, of course, by ω). The mutual inductance of the two circuits thus becomes identical with that given by equation (1).

Looking at the inductance of a shunt from this point of view we note the close analogy between four-terminal resistances and mutual inductances, and in what follows we shall use the term "four-terminal impedance" to cover both classes of apparatus. As we have seen, the voltage from the potential terminals of a shunt is not, in general, in exact phase with the current, and we shall see later that, owing to eddy currents and capacity effects, the secondary voltage of a mutual inductance is not always in exact quadrature with the primary current. To avoid circumlocution, a mutual inductance which does give a secondary voltage in quadrature with the primary current, or a shunt which has zero inductance, will be spoken of as "pure," and any departure from these ideal conditions will be described as an "impurity" in the four-terminal impedance considered.

These definitions may be summarized in mathematical form by considering a current

$$i = I_m \sin \omega t \tag{2}$$

to flow through the current terminals of a "four-terminal impedance." The voltage between the potential terminals may then be expressed by the equation

$$e = E_1 \sin \omega t + E_2 \cos \omega t \tag{3}$$

In the case of a shunt, we have the following definitions

resistance $$R = \frac{E_1}{I_m} \tag{4}$$

inductance $$L = \frac{E_2}{\omega I_m} \tag{5}$$

phase angle $$\theta = \tan^{-1} \frac{E_2}{E_1} = \tan^{-1} \frac{\omega L}{R} \tag{6}$$

time constant $$T = \frac{L}{R} = \frac{\tan \theta}{\omega} \tag{7}$$

In the case of a mutual inductance, the corresponding definitions are

mutual inductance $$M = \frac{E_2}{\omega I_m} \tag{8}$$

"resistance" $$R = \frac{E_1}{I_m} \tag{9}$$

and, since it is more convenient to handle small angles than angles near 90°, we will take as the

phase defect $$\tau = \tan^{-1} \frac{E_1}{E_2} = \tan^{-1} \frac{R}{\omega M} \tag{10}$$

time constant $$T = \frac{\tan \tau}{\omega} = \frac{R}{\omega^2 M} \tag{11}$$

IV. RELATIVE METHODS

1. CURRENT-TRANSFORMER METHOD

Measurements on the inductances of shunts may be divided into two classes: First, relative measurements in which the difference in time constant of two shunts is determined in terms of known quantities; and, second, absolute measurements in which the time constant of a single shunt is completely determined.

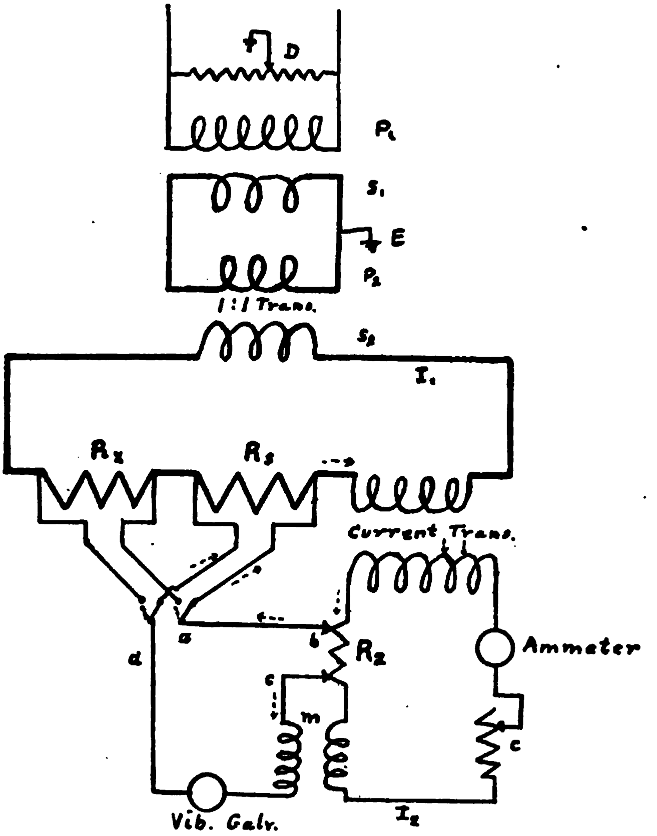


FIG. 3.—*Connections for current transformer method for comparing the time constants of two shunts*

A considerable variety of relative methods are available for the comparison of time constants. In addition to those mentioned on page 376 the most straightforward is perhaps the Thomson bridge as suggested by Dr. Wenner.[11] This, however, is very cumbersome in practice. The method which was used in most of this work and found very rapid and convenient may be called the

---

[11] Wenner, this Bulletin, 8, p. 559, 1912; also Sharp and Crawford, A. I. E. E. Trans., 29, p. 1537, 1910.

"current-transformer method." It is a substitution method and is a highly specialized form of a-c potentiometer. The connections are shown in Fig. 3. A suitable large current I_1 flows in series through the two shunts to be compared R_s and R_x and through the primary of a current transformer. The secondary of this transformer furnishes a current I_2 which supplies the "potentiometer circuit." The voltage drop in one of the shunts is balanced against the drop in a variable resistance R_2, and any necessary quadrature component is supplied by the small variable mutual inductance m. The condition of balance is indicated by a sensitive vibration galvanometer. It is evident from the vector diagram Fig. (4) that

$$\mu_s + \theta_s = \varphi + \theta_2 \tag{12}$$

and that

$$\mu = \tan^{-1}\frac{\omega m}{R_2} \tag{13}$$

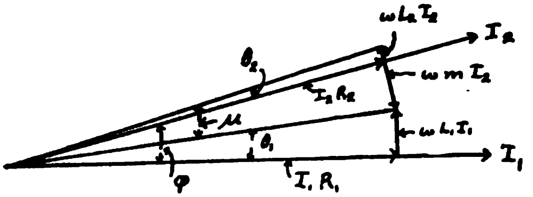


FIG. 4.—*Vector diagram of current transformer method*

where μ is the apparent phase angle of the transformer, φ the true phase angle of the transformer, and θ_s and θ_2 the phase angles of the resistances R_s and R_2, respectively. The subscript s is used here and in what follows to indicate the values observed when the standard shunt R_s is connected, while the subscript x is applied to values observed when the unknown shunt R_x is used.

If the balance is repeated, using R_x we have

$$\mu_x + \theta_x = \varphi + \theta_2'$$

hence eliminating φ

$$\theta_x - \theta_s = \mu_s - \mu_x + \theta_2' - \theta_2 \tag{14}$$

or

$$T_x - T_s = \frac{m_s}{R_2} - \frac{m_x}{R_2'} + T_2' - T_2 \text{ approx.} \tag{15}$$

It may be noted that if the time constants of R_s and R_2 are known, this becomes a convenient method of calibrating current transformers.[12]

---

[12] Sharp and Crawford, A. I. E. E., 29, p. 1537, 1910; Agnew and Silsbee, A. I. E. E., 31, p. 1267, 1912.

When the shunts R_s and R_x are not of equal resistance the second balance may be obtained in either of two ways. First, by simply increasing R_2, and, second, by changing the primary connections of the transformer from parallel to series. By making both these changes, shunts of very different resistance can be directly compared. The assumption made in the second method, that the phase angle of a well-designed transformer is a function of the secondary circuit conditions only, has been repeatedly justified by measurements at the Bureau of Standards. As a further check, shunts *E* and *H* having 0.005 and 0.0025 ohm, respectively, were compared by the two methods. The results given in Table 1 show an excellent agreement. Similar measurements at 700 cycles also agreed, showing that up to that frequency the electrostatic capacity between the windings does not affect the accuracy of the method. It is to be noted that by changing connections both shunts are kept at approximately their full current capacity and thus there is no loss of sensitivity if these capacities are different.

TABLE 1

Agreement in Difference of Time Constant of Shunts H=0.0025 Ohm and E=0.005 Ohm Obtained by (a) and (b) Changing R_2 and (c) Changing Ratio of Transformer.

Ratio	R_2	(T_x-T_s) obs.
	Ohms	Seconds
(a) 24:1	0.12 -0.060	9.89×10^{-6}
(b) 12:1	.060- .030	9.92
(c) 24:1-12:1	.060	9.93
Mean		9.91

A special transformer was built for these measurements with 10 primary coils. Each coil consisted of four parallel circuits spaced 90° apart around the core. The ratio and phase angle observed when any one coil was used as primary agreed with the values observed when all 10 coils were used in parallel, to within 1 part in 12 000 in ratio and within 0.3 minute in phase angle, even when operating at a secondary current of only 1 ampere. The variable resistance R_2 was of 10-ampere capacity and could be adjusted to 0.00001 ohm.[13] The mutual inductance was of the astatic type, which greatly reduced troubles from stray fields. The range needed for most work by this method is 0 – 5 microhenrys.

---

[13] For description of a similar resistance, see Agnew, this Bulletin, 7, p. 423; 1911 (Reprint No. 164).

Since the phase angle of the transformer does depend upon the frequency, current, and secondary resistance, care must be taken to keep these constant during the comparison. A compensating resistance C can be used to keep the total secondary resistance constant when R_2 is varied.

It is seen by equation (15) that the time constants of R_2 enter into the results. This is not serious, however, since R_2 is of comparatively high resistance and small current capacity. The time constant of the apparatus used was of the order of 0.1 microsecond, so that the change in this from one setting to another was very slight. The value of this inductance was computed from the dimensions and the corrections applied when necessary.

The time constant T_2 of this secondary resistance may be compared with that T_1 of the primary by using a transformer having a 1:1 ratio. Then, if the apparent phase angles μ_a and μ_b are observed, using first the usual connection and then one in which the primary and secondary resistances are interchanged, we get

$$T_1 - T_2 = \frac{\mu_b - \mu_a}{2\omega} \qquad (16)$$

The secondary resistances giving 0.05 and 0.10 ohm were compared with primary shunts M of 0.05 ohm and A_2 of 0.10 ohm, respectively, by this method. These measurements gave $T_M - T_{.05} = 0.82 \cdot 10^{-6}$ and $T_{A_2} - T_{0.10} = 2.26 \cdot 10^{-6}$ second. These results are included in the general adjustment of finally accepted values given below.

The sensitivity of the method is simply a matter of the current capacity of the shunt under test and the sensitivity of the galvanometer available. Since R_2 is small and the secondary winding of m can be made of low resistance, it is advisable to use a low resistance galvanometer. It is evident that under these circumstances the sensitivity is as good as it can ever be in any future normal use of the shunt with the same galvanometer. The galvanometer used in most of the work had an effective resistance of only 2 ohms and a sensitivity of 0.5 mm per microvolt at 60 ~.

The most troublesome source of error is, of course, stray fields. These, however, can be made small by keeping the heavy current circuits at a distance and then eliminated by reversing connections, etc. Another rather unexpected trouble is charging currents. These arise from two sources. First, the relatively high voltage, say 100 volts, used to supply the power to the primary of the step-down transformer can send sufficient charging current through the capacity of the various transformer windings to cause serious trouble. This can be avoided by (*a*) grounding the source through a slide wire *D* (see Fig. 3) and adjusting the potentials until the effect stops, or (*b*) by using a low voltage 1 : 1 transformer and grounding the primary as at *E*. A sensitive test for this effect is to open the galvanometer circuit on one side as at *a* and then ground the secondary circuit, say at *c*. Any charging current will then flow through the galvanometer and produce a deflection. The other source of charging current is the primary of the current transformer. Currents circulate as shown by the dotted arrows, Fig. 3, and in part flow through the galvanometer. This trouble occurs only when small currents and consequently high impedances are used. It may be made negligible by keeping the side *ab* of the galvanometer circuit of lower resistance than *cd*. Since the time constants to be measured are small and usually needed to only a few per cent, there is no difficulty in calibrating *m* to a sufficient accuracy.

From changes in temperature, etc., the phase angle of the transformer may drift slightly during the measurements. By taking a symmetrical series of runs, first on the standard and then the unknown and vice versa, this drift can be very effectually eliminated.

In the course of this work a group of 12 shunts, some of which had several pairs of potential leads, forming the equivalent of 19 shunts, were repeatedly intercompared by this current-transformer method, making altogether some 60 difference measurements. The 19 time constants were adjusted by a series of weighted averages to best fit the 60 differences. A least-square method, while theoretically more exact, would have been extremely laborious. The various individual differences were found to agree with the differences computed from the adjusted values with an average deviation of $0.05 \cdot 10^{-6}$ second. This adjustment gave, of course, only relative values of the time constants, one shunt being arbitrarily set equal to zero. A list of the shunts with their dimensions, etc., is given in Table 2.

TABLE 2

Constants and Dimensions of the Shunts used

Shunt	Resistance	Current capacity	L	T	Material	Spacing center to center	Thickness	Width (or diameter)	Length	Remarks
	Ohms	Amp.	Henrys	Seconds		cm	cm	cm	cm	
M	0.05	20	44.0×10^{-9}	0.88×10^{-6}	Manganin					Old working standards of Bureau of Standards; built about 1903.
L	.01	50	28.0	2.80	do					
H	.0025	100	29.3	11.71	do					
Rq	.001	200	12.77	12.77	do					
S	.001	500	10.72	10.72	do					
G	.00025	1000	2.95	11.83	do					
A_2	.0998	10	247.0	2.47	Kulmiz	0.457	0.200		34.93	Three pairs of potential leads on parallel wire. Computable standard.
A_3	.0499	10	120.0	2.41	do	.449	.200		17.48	
A_4	.01045	10	28.4	2.72	do	.486	.200		3.52	
E_1	.00793	150	15.0	1.89	Manganin	.140	$.106_4$		54.78	Three pairs of potential leads on flat strip. Computable standard.
E_2	.00510	150	8.89	1.74	do	.140	$.106_4$	4.986	35.62	
E_3	.00104	150	1.85	1.78	do	.140	$.106_4$		7.18	
F_2	.00098	350	10.1	10.35	Brass	.127	$.104_0$	4.976	35.92	Mate to E.
N_i	.00198	250	− 1.51	− .76	Benedict nickel	Concentric tubes working one inside.	.080	1.910	41.4	Dimensions are for inner tube. Potential leads in inside.
N_o	.00198	250	+45.1	22.78	do		.090	3.180	41.4	Dimensions are for outer tube. Potential leads outside of outer tube.
T_{12}	.001016	250	− .57	− .56	do					
T_{23}	.001017	250	− .50	− .49	do		.077	1.908	16.8	Potential leads inside inner tube. Computable standard.
T_{13}	.002033	250	− 1.06	− .52	do					
Q	.0015	100	8.5	+5.7	Copper	0.059	.0365	2.07	30.0	Flat strip.
P	.0005	400	− 2.2	−4.4	do		.07	.63	26.5	Inner concentric tube.
C	.000337	350	7.4	21.95	do	.094	.0839	4.02	32.1	Flat strip.
K	.01	60	8.3	.83	Kulmiz	.093	.0836	3.99	32.1	Mate to C.

Though commercial current transformers are built only with a ratio of primary to secondary currents greater than unity, the method may be extended to shunts of less than 5-ampere capacity by using a power transformer of suitable rating. The system of differences described above was connected with a 1-ohm standard, which had been measured by Dr. Curtis of the Bureau of Standards by two-terminal methods, by such an arrangement. Using a 2 kw 1100:2200/110-volt transformer as a step-up current transformer this 1-ohm was compared with the 0.1-ohm shunt A_2. The difference of their time constants was found to be

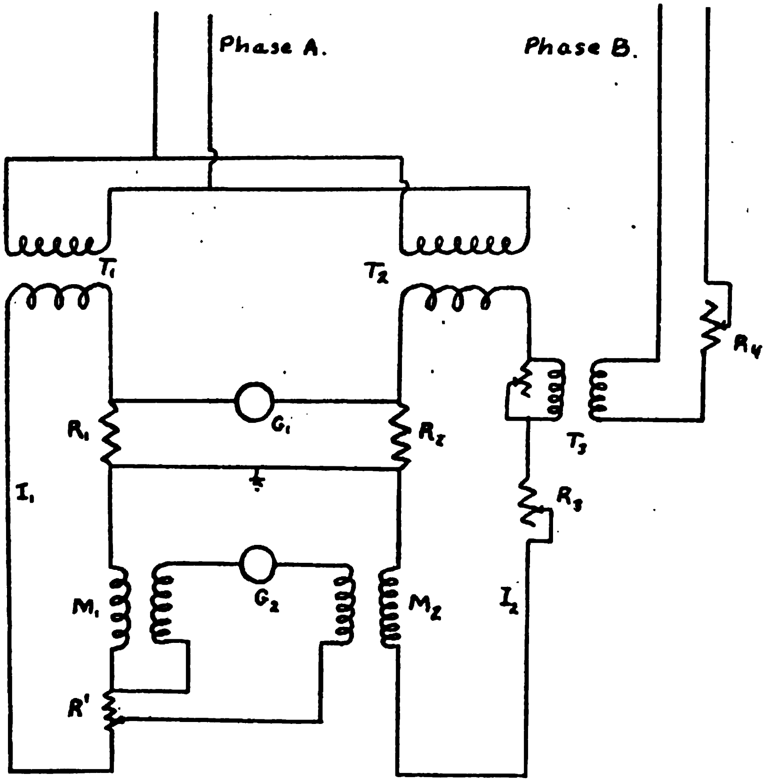


FIG. 5.—*Connections for mutual inductance method for comparing the phase angles of two shunts*

$$T^{A}_{2} - T_{1\Omega} = 2.24 \times 10^{-6}$$

This is in good agreement with the computed value of $2.18 \cdot 10^{-6}$ seconds. The results of this comparison are included in the final adjustment in Table 9.

2. MUTUAL-INDUCTANCE METHOD

A second relative method was tried in this work. It is also of the potentiometer type, but involves a simultaneous balance on the standard and unknown shunts instead of a substitution of one for the other. The connections are shown in Fig. 5. Here R_1 and R_2 are the shunts under test and M_1 and M_2 two mutual inductances. Phase A of a two-phase generator supplies through two transformers T_1 and T_2 the currents I_1 and I_2 which are approximately in the same phase. The other phase, B, excites the small transformer T_3 and thus inserts into the secondary of T_2 a variable out-of-phase component and permits of a sensitive control of the relative phases of I_1 and I_2. The magnitude of I_2 is regulated by the resistance R_8.

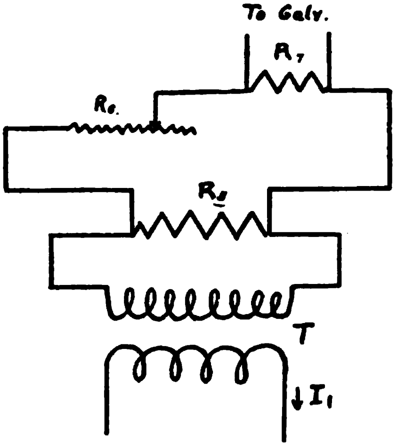


FIG. 6.—*Connections for obtaining a very small adjustable resistance*

The procedure is for one observer to control R_4 and R_8 until G_1 shows a balance while the other observer varies R' and M_1 until G_2 is balanced. When such a simultaneous balance has been obtained we have, neglecting terms of higher order, the relations:

$$\frac{M_1}{M_2}=\frac{R_1}{R_2} \tag{17}$$

$$\frac{L_2}{R_2}-\frac{L_1}{R_1}=\frac{R'}{\omega^2 M_1}+\frac{1}{\omega}(\tau_1-\tau_2)^{14} \tag{18}$$

The voltages in the circuit of galvanometer G_1 are determined by the permissible voltage on the shunts, and G_1 should have as low resistance as possible. The magnitudes of M_1 and M_2, however, are arbitrary, subject to equation (17). Hence, this circuit can be designed to give higher sensitivity than the other and therefore will introduce no observational errors in the result. The resistance R' must be very small. The equivalent of a very small resistance can most easily be obtained by the arrangement shown in Fig. 6. If R_5 and R_7 are small compared with R_6 we have

$$R'=\frac{R_7 R_5}{R_6}\cdot\frac{1}{P}$$

---

[14] τ_1 and τ_2 are the phase defects of M_1 and M_2 as defined by equation (10), p. 381.

where P is the ratio of the current transformer T. The transformer is not essential, but helps reduce R' and also insulates the galvanometer circuit and greatly reduces stray charging currents. The effect of the phase angle of the transformer is entirely negligible. In making a setting care should be taken to vary R_6 and *not* R_7. Otherwise, the change in sensitivity may lead to an entirely false minimum.

Stray fields and charging currents must, of course, be guarded against as in all work of this kind. A more serious source of error is the correction $(\tau_1-\tau_2)$ due to the phase defects of the mutual inductances used. If the two shunts are of equal resistance, the inductances may be interchanged and the correction thus determined. The determination of this correction in the general case will be discussed more fully later.

Four difference measurements were made by this method and the results are given in Table 3, together with the values computed from observations by the current-transformer method. It is seen that this mutual-inductance method is not as precise as the former, but that there is no constant discrepancy greater than the experimental error of the latter. The lack of precision is probably due to the continual variations in resistance of the two heavy current circuits caused by self-heating, drafts, etc. This fluctuation requires the observers to be constantly alert and makes the simultaneous balance rather difficult.

TABLE 3

Results of Relative Measurements by Mutual-Inductance Method

Shunts compared	(T_1-T_2) Mutual inductance method	(T_1-T_2) Current transformer method	Difference
	Microseconds	Microseconds	Microseconds
R-S	2.1	2.0_5	$+0.0_5$
G-T_{13}	12.1	12.3_5	$-.2_5$
G-L	9.0	9.0_3	$-.0_3$
L-T_{13}	3.8	3.3_2	$+.4_8$

V. ABSOLUTE METHODS

The best method for the determination of the inductance of a shunt is by comparison with some four-terminal standard whose inductance can be computed from the dimensions. This method, which is the only one hitherto used, is open to the objection that in the computed standard the current distribution, end effects, etc., may not be such as are assumed in the mathematical theory. In the work described below each type of standard was carefully studied with a view to these sources of error. Also three distinct types were used and the probability of the same error occurring in all is very remote. Nevertheless, it was thought advisable to use two other methods recently proposed,[15] in which there is no dependence on computation.

1. COMPUTATION

There are many forms of circuit, the inductance of which can be computed from the shape and dimensions of the conductors. For the purpose of this investigation, however, where it was necessary to keep the ratio $\frac{L}{R}$ small, the available forms are all of the type of two parallel straight conductors, long in comparison with their cross section and spacing.

Formulas for the inductance of such circuits have been given by Gray,[16] Rosa,[17] Orlich,[18] and others. For shunts of type I in which the resistance material forms a nearly closed circuit, these formulas are special cases of the general expression

$$L = 2\ l\ (2 \log D_{12} - \log D_{11} - \log D_{22}) \qquad (19)$$

where D_{12} is the geometric mean distance of the cross-sectional areas of the conductors from each other and D_{11} and D_{22} the g. m. d's of each area from itself. For shunts of type II it is necessary to either build up the inductance piecemeal as indicated by equation (1) or to regard it as the limit of the mutual inductance of two circuits which coincide over a part of their length.

These formulas are deduced on the assumption that the current is uniformly distributed over the cross section of the conductor. That this limitation is not as serious as appears at first sight is shown by the followng reasoning: The emf induced by the magnetic field is not in general the same at different points in the cross section of the conductor and therefore the current density will not be uniform over the section. The resulting current distribution may be looked upon as made up of a system of eddy currents superposed on a uniform distribution. The net effect of the resistance drop due to these currents and the induced emf must be to make the planes perpendicular to the axis equipotential.

---

[15] Wenner, Weibel, and Silsbee, this Bulletin, 12, p. 11; 1915 (Reprint No. 246).

[16] Gray, Absolute Measurements, Vol. II, Part I, p. 288.

[17] Rosa, this Bulletin 4, p. 321, 1907; Rosa and Grover, this Bulletin 8, p. 150, 1911.

[18] Orlich, Kapazität und Induktivität, p. 68.

If this is the case the quadrature component of the resultant potential difference per unit length is

$$e_0 = e - i_e \rho \tag{20}$$

where e is the induced linear emf, i_e the eddy-current density, and ρ the resistivity. Multiplying by dS and integrating over the whole cross section of the conductor

$$\int e_0 \, dS = \int e dS - \int \rho i_e \, dS \tag{21}$$

but since i_e is merely the eddy-current density $\int i_e dS$ must vanish

$$\therefore e_0 = \frac{\int e dS}{S} \tag{22}$$

This area average of induced emf is what is given by the geometric mean distance formulas and they are therefore valid even if the increase in resistance due to skin effect is appreciable provided only that the magnetic effects of the eddy currents are negligible.

It is sometimes more convenient to go back to this area average of emf in computing inductances than to use geometric mean distances, and this method will be used in developing the formulas for tubular shunts given below.

(*a*) **Parallel Wire Type.**—For the case of parallel wires equation (19) becomes

$$L = 4\, l \left(\log \frac{d}{a} + \frac{1}{4} \right) \tag{23}$$

d = spacing of wires center to center
a = radius of wire.

This formula assumes uniform current distribution over the cross section, but there is little liability to error from this source at commercial frequencies. Any nonhomogeneity due to the process of drawing would leave the resistivity symmetrical about the axis and affect only the small second term.

Shunt "A" was constructed of Kulmiz alloy wires 0.200 cm in diameter and spaced 0.457 cm center to center. Pairs of potential leads were attached at distances of 3.52, 17.5, and 35 cm from the closed end. Difference measurements were made by the current transformer method and showed that the end effects were entirely negligible. Table 4 gives in the second column the values of T computed from the dimensions and the observed resistance assuming an undetermined inductance ΔL to represent the end effect. Comparing the differences of these values with the observed differences, we see that setting ΔL equal to zero gives the best agreement.

TABLE 4

Results on Shunt A

Pot leads	Time constant, calculated	Difference, calculated	Difference, observed
	Microseconds	Microseconds	Microseconds
A_2	$2.47+0.01\Delta L$	$+0.03-0.01\Delta L$	+0.06
A_3	$2.44+.02\Delta L$	$-.30-.08\Delta L$	−.31
A_4	$2.74+.10\Delta L$		

(*b*) **Flat Strip Type.**—In the case of parallel rectangular conductors the exact formula[19] obtained from equation (19) is inconvenient, not only because of the large number of terms, but also because the result appears as the difference of large terms, which must, therefore, be computed with great accuracy. By expanding in series, however, it can be put in the much more convenient form[20]

$$L=4l\left[\frac{\pi}{3}(3\beta-\delta)-\frac{25}{12}\beta^2-\frac{1}{12}\beta^4-\frac{1}{12}\beta^2\delta^2 \;.\;.\;.\;.\;.\right.$$
$$\left.+\frac{1}{12\delta^2}\left\{\alpha^4\log\alpha-2\beta^4\log\beta+\gamma^4\log\gamma-2\,\delta^4\log\delta\right\}\right] \tag{24}$$

Here

$$\alpha=\frac{2\,b+g}{w},\ \beta=\frac{b+g}{w},\ \gamma=\frac{g}{w},\ \delta=\frac{b}{w}$$

where

w = width of strip
b = thickness of metal
g = thickness of insulator
l = length of circuit

The terms neglected in this formula are of the order β^6.

In case the strips are of unequal thickness we have the analogous expression[21]

$$L_1=2\,l\left[\pi\left(\gamma+\frac{\eta}{2}+\frac{\delta}{6}\right)-25\left(\frac{\gamma\alpha}{12}+\frac{\eta^2}{36}+\frac{\delta\eta}{24}+\frac{\delta^2}{72}\right)\;.\;.\;.\;.\;.\right.$$
$$\left.+\frac{1}{12\delta\eta}\left(\alpha^4\log\alpha-\kappa^4\log\kappa-\lambda^4\log\lambda+\gamma^4\log\gamma-2\delta^3\eta\log\delta\right)\right] \tag{25}$$

---

[19] The value of D_{12} is given by Rosa, this Bulletin 8, p. 6 eq. (8), and for D_{11}, this Bulletin 8, p. 167 eq. (124).

[20] An equivalent form is given by Orlich (Zs. für Instrumentenkunde 29, p. 241; 1909), together with a table of values of $x^4 \log x$, which is useful in computing the last term. The formula may be obtained by substituting into eq. (19) the proper values of D_{12} and D_{11}. The series expansion is obtained by expressing the logarithmic and antitrigonometric terms as power series in α, β, etc. The terms may then be combined and the higher powers neglected.

[21] The derivation of this equation is similar to that of eq. 24 except that the values for the geometric mean distance are substituted in $L_1=2\,l\log\frac{D_{12}}{D_{11}}$, since the inductance of a single strip is desired instead of that of the return circuit.

Here L_1 is the inductance of the strip having thickness b with return in the other strip, where

$$\alpha=\frac{b+c+g}{w},\ \gamma=\frac{g}{w},\ \delta=\frac{b}{w},\ \eta=\frac{c}{w}$$

$$\kappa=\frac{b+g}{w},\ \lambda=\frac{c+g}{w}$$

where

w = width of strips
b = thickness of strip used
c = thickness of return conductor
g = thickness of insulator
l = length of circuit.

An interchanging of the letters δ and η gives, of course, the inductance L_2 of the other strip. The inductance of the complete circuit is then the sum L_1+L_2.

These formulas were used in computing the corrections for the inductance of the secondary resistance R_2 mentioned on page 385 above.

A standard shunt E was constructed of sheet manganin 0.106 cm thick, 4.99 cm wide, and about 60 cm long. The strips were clamped firmly together with 0.035 cm of paper insulation between. Pairs of potential leads were attached at distances 7.2, 35.6, and 54.8 cms. from the closed end, giving resistances of 0.001, 0.005, and 0.008 ohm, respectively.

The sources of error to be guarded against in a shunt of this type are (1) skin effect, (2) nonuniform current distribution due to lack of homogeneity, (3) inductive effects in the potential leads, (4) end effects. These points will be considered in order. Bethenod,[22] Orlich,[23] and others have computed the effect of nonuniform current distribution on the resistance and inductance of a circuit of this shape assuming the length and width of the plates both infinite. The latter assumption seems a little startling, but since the strips are close together the magnetic field is nearly constant over most of the width. The nonuniform distribution edgeways is confined to a slight excess of current over a region at the edge only a few per cent of the width of the plate. These formulas show that for the frequencies and materials used the skin effect is entirely negligible.

A more serious possibility is the danger of nonuniform current distribution due to accidental causes, such as poor solder, where the current leads are attached and nonhomogeneity in the material itself. If, for example, the current tended to flow in the upper edge of one sheet and the lower edge of the other, this would seriously alter the inductance. The theoretical formula for the change in linear inductance of two infinitely thin strips of width w and spacing d when displaced transversely a distance y is

---

[22] Resistance of Thin Plates to alternating currents, Jahr. d. Drahtloser Tel., 2, p. 397.

[23] Zeitschrift für Instrumentenkunde, 29, p. 241; 1909.

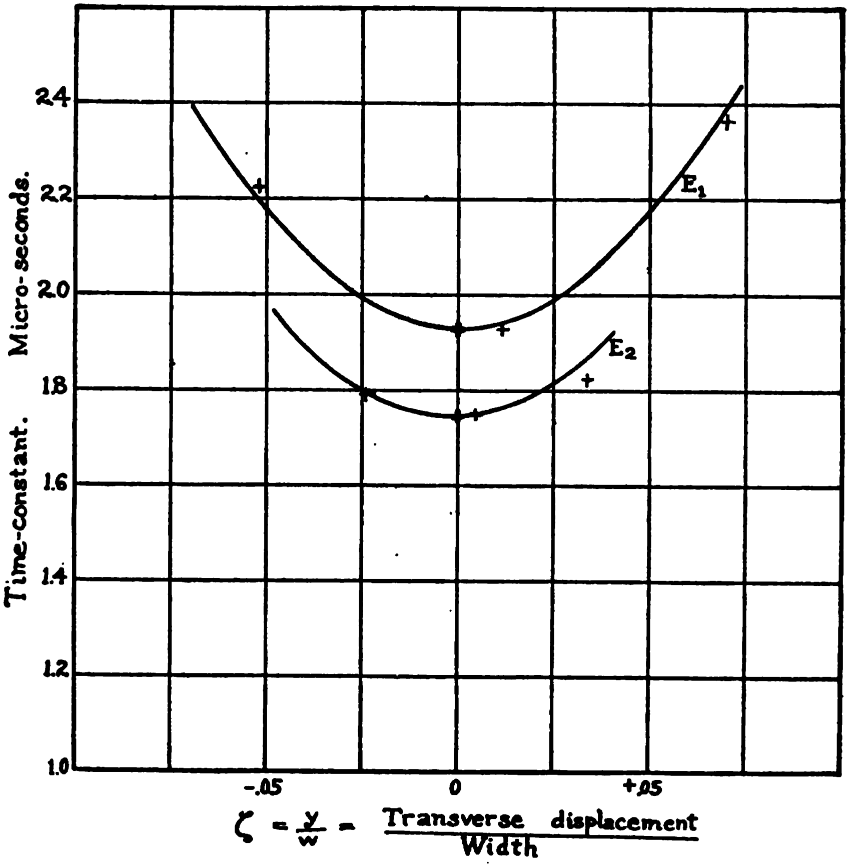


FIG. 7.—*Effect of transverse displacement on inductance of flat strip shunt. Curves are computed, crosses are observed points*

$$\Delta L = 4\,l\left[\frac{3}{2}\zeta^2 - \frac{1}{2}(\zeta^2 - \beta^2)\log(\zeta^2 + \beta^2) - \beta^2 \log \beta - 2\beta\zeta \tan^{-1}\frac{\zeta}{\beta}\right] \qquad (26)$$

where $\zeta = \frac{y}{w}$ and $\beta = \frac{d}{w}$. This effect always tends to increase the inductance, and the procedure adopted was to slide the strips past each other (by slightly springing the closed end) and measure the inductance in each position. The curves on Fig. 7 are computed from eq (26) and the crosses (+) are the observed points. They seem to indicate that the true zero, where the currents most nearly neutralize, is slightly to the right of the mechanical zero. The difference is very slight, however, and was neglected. Though this agreement of the theoretical and observed values is of course no proof that the current is uniformly distributed, it indicates that such is probably the case.

The end effects and mutual inductance errors were handled in the same manner as with shunt A. The difference measurements gave

$$T_{E_1} - T_{E_2} = 0.17 \cdot 10^{-6} \text{ sec.}$$
$$T_{E_3} - T_{E_2} = 0.04 \cdot 10^{-6} \text{ sec.}$$

The first difference is probably due to mutual inductance between the current and potential leads. Since the leads E_2 were seven times as far from the current leads as E_1, any such effect in E_2 would be entirely negligible. The second difference is practically negligible and brings out the fact that the formulas given above hold for shunts nearly as short as their width, provided the spacing is close.

To determine the precision required in measuring the dimensions of the shunt, equation (24) may be written in the approximate form

$$L = 4\pi \frac{l}{w}\left(a - \frac{4}{3} b\right) \tag{27}$$

where the over-all dimension a and the thickness of metal b are the dimensions most easily measured. By differentiating we obtain

$$\frac{dL}{L} = \frac{da}{a} \cdot \frac{1}{1 - \frac{4}{3} \cdot \frac{b}{a}} \tag{28}$$

and

$$\frac{dL}{L} = -\frac{db}{b} \cdot \frac{1}{\frac{3}{4} \cdot \frac{a}{b} - 1} \tag{29}$$

In the limiting cases of $b = 0$ and $b = \frac{a}{2}$

these become

$$\frac{dL}{L} = \frac{da}{a} \cdot 1 \quad \text{and} \quad \frac{dL}{L} = \frac{da}{a} \cdot 3 \tag{30}$$

and

$$\frac{dL}{L} = -\frac{db}{a} \cdot \frac{4}{3} \quad \text{and} \quad \frac{dL}{L} = -\frac{db}{b} \cdot 2 \tag{31}$$

respectively. The percentage error in L is therefore at worst three times the percentage error in the measurement of a and twice the percentage error in b. Since these may be conveniently measured to a fraction of 1 per cent with micrometer calipers, they are not particularly serious sources of error.

(*c*) **Tubular Type.**—The third type of shunt which can be used as a computable standard consists of a pair of concentric tubes one or both of which are of resistance material. The potential leads may be arranged in a number of different ways yielding correspondingly different values of the four-terminal inductance. The formulae for the various cases are so similar in appearance and the self and mutual inductive effects so superposed that an analysis from the closed-circuit point of view is very confusing. The following discussion will separate the various sources of emf and obtain any particular case by a summation of the proper effects.

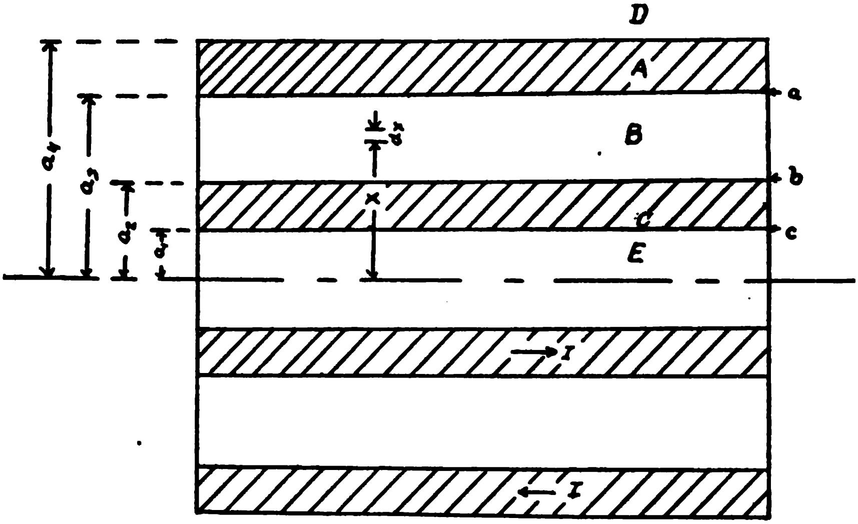


FIG. 8.—*Cross section of tubular shunt*

Fig. 8 represents a longitudinal section of unit length of such a pair of concentric tubes. Let the radii be a_1, a_2, a_3, and a_4 from inside outward,

$$\left.\begin{array}{ll}\text{and let us define} & s=\dfrac{a_4-a_3}{a_4}\\[2ex] \text{and} & t=\dfrac{a_2-a_1}{a_2}\\[2ex] \text{and} & u=\dfrac{a_3-a_2}{a_3}\end{array}\right\} \qquad (32)$$

If a current I flows to the right in the inner tube and returns in the outer, the magnetic flux densities H_D, H_A, etc. (assuming $\mu = 1$ and the tubes infinitely long) in the regions D, A, B, C, E are, respectively,

$$\left.\begin{aligned} H_D &= 0 \\ H_A &= \left\{\frac{2}{x} - \frac{2\,(x^2 - a_3^2)}{x\,(a_4^2 - a_3^2)}\right\} I \\ H_B &= \frac{2}{x} I \\ H_C &= \frac{2\,(x^2 - a_1^2)}{x\,(a_2^2 - a_1^2)} I \\ H_E &= 0 \end{aligned}\right\} \tag{33}$$

Where x is the distance from the axis to the point considered. It will be convenient to split H_A into two parts, H_{AI}, due to the current in the inner, and H_{AO}, due to the outer conductor. Where

$$\begin{aligned} H_{AI} &= \frac{2}{x} I \\ H_{AO} &= -\frac{2\,(x^2 - a_3^2)}{x\,(a_4^2 - a_3^2)} I \end{aligned} \tag{34}$$

Integrating equations (33) over their respective areas gives us the complete flux linking a conductor just inside each area, which we may denote by ϕ_{AO_a}, etc., i. e., the flux in A due to current in the outer conductor and linking a wire at a. We thus obtain

$$\begin{aligned} \phi_{AO_a} &= \int_{a_3}^{a_4} H_{AO}\, dx = \left[-1 + \frac{2a_3^2}{a_4^2 - a_3^2} \log \frac{a_4}{a_3}\right] I \\ &= \left(-s - \frac{s^2}{6} + \frac{s^4}{30} \cdots\right) I \end{aligned} \tag{35}$$

$$\phi_{AI_a} = \int_{a_3}^{a_4} H_{AI}\, dx = \left[2 \log \frac{a_4}{a_3}\right] I = \left(2s + s^2 + \frac{2}{3} s^3 \cdots\right) I \tag{36}$$

$$\phi_{BI_b} = \int_{a_2}^{a_3} H_{BI}\, dx = \left[2 \log \frac{a_3}{a_2}\right] I = \left(2u + u^2 + \frac{2}{3} u^3 \cdots\right) I \tag{37}$$

$$\phi_{CI_c} = \int_{a_1}^{a_2} H_{CI}\, dx = \left[1 - \frac{2a_1^2}{a_2^2 - a_1^2} \log \frac{a_2}{a_1}\right] I = \left(+t + \frac{t^2}{6} - \frac{t^4}{30} \cdots\right) I \tag{38}$$

We shall also need expressions for ϕ_{AOA}, i. e., average linkages of the flux in A due to the outer current linking the conductor A

and producing an average voltage as defined above. These expressions are given by

$$\phi_{AOA}=\frac{1}{\pi(a_4^2-a_3^2)}\int_{a_3}^{a_4}2\pi x\,dx\int_{x}^{a_4}H_{AO}\,dx$$
$$=\left[-\frac{a_4^2-3a_3^2}{2(a_4^2-a_3^2)}-\frac{2a_3^4}{(a_4^2-a_3^2)^2}\log\frac{a_4}{a_3}\right]I \tag{39}$$
$$=\left(-\frac{2}{3}s+\frac{1}{15}s^3+\frac{s^4}{20}\cdots\right)I$$

$$\phi_{AIA}=\frac{1}{\pi(a_4^2-a_3^2)}\int_{a_3}^{a_4}2\pi x\,dx\int_{x}^{a_4}H_{AI}\,dx$$
$$=\left[-\frac{2\,a_3^2}{a_4^2-a_2^2}\log\frac{a_4}{a_3}+1\right]I=\left(+s+\frac{s^2}{6}-\frac{s^4}{30}\cdots\right)I \tag{40}$$

$$\phi_{CIC}=\frac{1}{\pi(a_2^2-a_1^2)}\int_{a_1}^{a_2}2\pi x\,dx\int_{x}^{a_2}H_{CI}\,dx$$
$$=\left[\frac{a_2^2-3a_1^2}{2(a_2^2-a_1^2)}+\frac{2\,a_1^4}{(a_2^2-a_1^2)^2}\log\frac{a_2}{a_1}\right]I=\left(\frac{2}{3}t-\frac{t^3}{15}-\frac{t^4}{20}\cdots\right)I \tag{41}$$

It may be noted that $\phi_{AO_a}=-\phi_{AIA}$ as should be the case since they are expressions for the mutual inductance between the same pair of conductors. In each of these equations the approximate expression in s, t, or u may be obtained by a simple series expansion. Since in practice the tubes used are always thin in comparison with their radii, these approximate expressions are sufficiently accurate and very convenient.

Considering now a few special cases, let us first take the ordinary "concentric main," as in Fig. 9*a*, where both tubes are used as resistance material and the potential leads are in the same transverse plane. Adding the various linkages with regard to their directions we get

$$L_a=\left[\phi_{CIC}+\phi_{BIb}+\phi_{AI_a}-\phi_{AOA}+2\phi_{AO_a}\right]\frac{l}{I}$$
$$=l\left[-\frac{a_2^2+a_1^2}{2(a_2^2-a_1^2)}-\frac{a_4^2+a_3^2}{2(a_4^2-a_3^2)}+\frac{2\,a_1^4}{(a_2^2-a_1^2)^2}\log\frac{a_2}{a_1}\right. \tag{42}$$
$$\left.+\frac{2\,a_4^4}{(a_4^2-a_3^2)^2}\log\frac{a_4}{a_3}+2\log\frac{a_3}{a_2}\right]$$

or

$$L=l\left[\frac{2}{3}\,t+2\,u+\frac{2}{3}\,s+u^2+\frac{2}{3}\,s^2\cdots\right]\text{(approx.)} \tag{42a}$$

This formula is identical with that deduced by Russell and others. This form of shunt, however, is not well adapted for use as a standard, since it requires two soldered joints between the potential terminals, and also there is an end correction which must be obtained experimentally.

A better arrangement is to use either the outer or inner tube separately, thus forming a shunt of the second type. In the latter case the potential leads may be brought out either radially through insulated openings in the outer tube as in 9 (*c*) or axially as in 9 (*d*). The inductances per unit length in the three cases are

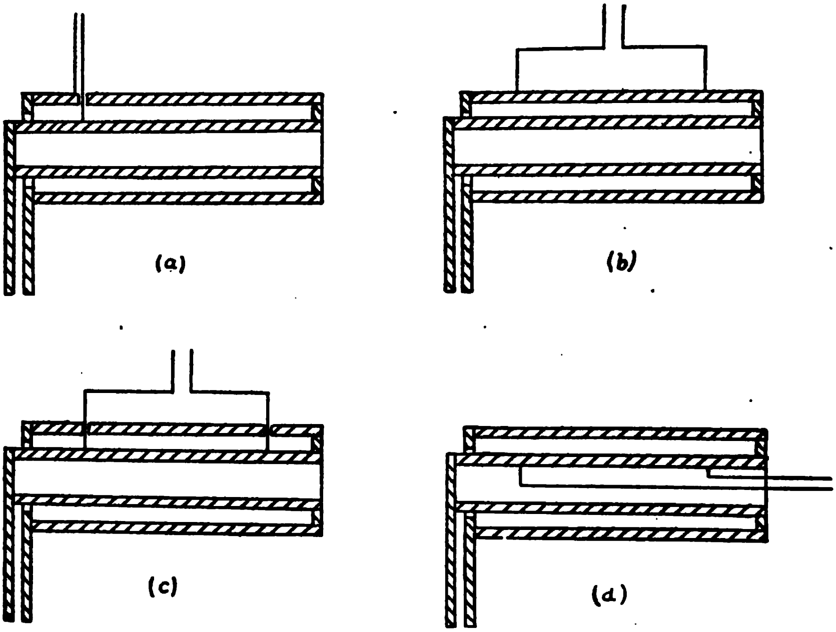


FIG. 9.—*Various arrangements of potential leads in tubular shunts*

$$L_{(b)} = \left[-\phi_{AIA} - \phi_{AOA} \right] \frac{l}{I} = \left(-\frac{1}{3}s - \frac{1}{6}s^2 \cdots \right) l \tag{43}$$

$$L_{(c)} = \left[\phi_{CIC} + \phi_{BIb} + \phi_{AO_a} + \phi_{AI_a} \right] \frac{l}{I}$$
$$= \left(s + \frac{2}{3}t + 2u + \frac{5}{6}s^2 + u^2 \cdots \right) l \tag{44}$$

$$L_{(d)} = \left[\phi_{CIC} + \phi_{BIb} + \phi_{AO_a} + \phi_{AI_a} - \phi_{CI_c} - \phi_{BIb} - \phi_{AI_a} - \phi_{AO_a} \right] \frac{l}{I}$$
$$= \left[\phi_{CIC} - \phi_{CI_c} \right] \frac{l}{I} = \left(-\frac{t}{3} - \frac{t^2}{6} \cdots \right) l \tag{45}$$

It may be noted that both L_b and L_d are negative and smaller in magnitude than L_a or L_c. L_c is also of interest because, although the working material does not form a closed circuit and the shunt properly belongs in the second type, yet there is no electromotive force induced in the potential leads.

A shunt N was constructed with a "Benedict nickel" tube inside a brass return tube, and so arranged that they could be shifted transversely. The resistance was about 0.002 ohm. Two sets of potential leads were used. "N_o" arranged as in Fig. 9 (*c*) and "N_i" as in (*d*). The inductances of the two arrangements were 45.1×10^{-9} henry and -1.5×10^{-9} henry, respectively.

At first sight it would appear that the inductance would be affected by any eccentricity of the tubes, but since the geometric mean distance of a point inside a circular annulus is independent of the position of the point it is evident from equation (19) that the inductance is also independent of eccentricity. This assumes that the current in the outer tube is uniformly distributed and that the tube is circular. The latter requirement is readily met by commercial tubing, but the former is difficult to obtain.

If the distribution in both tubes is uniform around the circumference, there is no magnetic flux inside the inner tube, and therefore an exploring coil inserted in this tube forms a very sensitive test for such a lack of uniformity. Shunt N showed a magnetic field at the center equivalent to that at a distance of 1 cm. from a wire carrying 3 per cent of the full current. This nonuniformity could not be eliminated by filing the ends of the outer tube and was probably due to lack of homogeneity in the brass. Since the inner potential leads were placed at the axis of the tube even this field should have had no effect on the inductance. This was corroborated by the fact that an extra current equal to 10 per cent of the main current flowing in an auxiliary wire just outside the shunt produced a barely detectible effect.

The effect of eccentricity was also investigated with this shunt, but a displacement as great as 1.5 mm showed no change in the time constant of N_i greater than 0.05 microsecond.

Heaviside[24] has shown that the rate of change in inductance of a concentric main with frequency is very small, involving only terms of the third order. Shunt T was also constructed in this shape, but using a copper tube of very uniform cross section as the return. The lack of uniform current distribution was found to be only one-third as serious as with shunt N and the inductance is believed to be very closely equal to the theoretical value.

---

[24] Electrical Papers, 2, p. 192.

2. QUARTER-PHASE METHOD

Though the values of inductance obtained from computable standards were believed to be correct, it was considered advisable to obtain an independent check if possible. Two such direct methods of measurement had been suggested by Dr. Wenner and Mr. Weibel of the Bureau of Standards and were tried out in some preliminary measurements in conjunction with the author.[25]

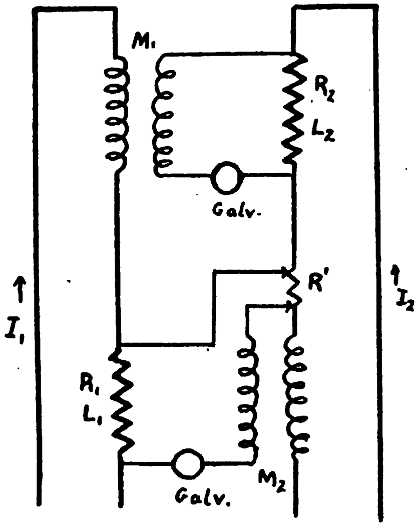


Fig. 10.—*Connections for quarter-phase method for measuring the inductance of shunts*

The first of these methods gives the sum of the time constants of the two shunts to be compared. The connections are shown in Fig. 10. M_1 and M_2 are mutual inductances whose primary windings have the same current carrying capacity as the shunts. The two circuits *A* and *B* are excited by alternating currents approximately in quadrature, and the values of *M* and R' and the relative phase and magnitude of I_1 and I_2 are adjusted until a simultaneous balance on both galvanometers is obtained. We then have neglecting small terms the two relations

$$R_1R_2 = \omega^2 M_1 M_2 \tag{46}$$

$$\frac{L_1}{R_1} + \frac{L_2}{R_2} = \frac{R'M_1}{R_1R_2} - \frac{1}{\omega}(\tau_1 + \tau_2) \tag{47}$$

By using three shunts and measuring the three sums of the time constants the resulting independent equations may be solved for the time constants of the individual resistances.

This method differs from the mutual-inductance method, described above, in the fact that here the drop in a resistance is balanced against the secondary voltage of a mutual inductance, while in the former case the two shunts are balanced against each other. The result of this is that the balance is extremely sensitive to slight changes in frequency and the unsteadiness caused by fluctuations in the speed of the driving motor is the practical limit to the sensitivity of the arrangement.

---

[25] This Bulletin, 12, p. 11; also Phys. Rev., 4, p. 71, 1914.

Both methods require a knowledge of the phase defects "τ" of the mutual inductances used. The values obtained in the preliminary work referred to above were based on certain values of τ, which further investigation has shown to be incorrect. The results of a recomputation of the quarter-phase measurements using the new values of τ are given in Table 5. The four time constants which best fitted the observed sums in column II were found and column IV computed from these values. The results are thus seen to be consistent to about 0.5 microsecond, which is probably better than could be normally expected without careful attention to speed control.

TABLE 5

Summary of Quarter-Phase Method

I Shunts	II Obs. sum	III Weights	IV Comp. sum	V Obs.—comp
	Microsec.		Microsec.	Microsec.
T_C+T_K	22.8	4	22.6	+0.2
T_C+T_R'	35.8	2	36.1	−.3
T_C+T_S'	32.4	1	32.9	−.5
$T_R'+T_K$	16.2	2	16.3	−.1
$T_S'+T_K$	12.4	1	13.0	−.6
$T_R'+T_S'$	27.0 26.2	1 2	26.5	+.5 −.3

The shunts S' and R' are not comparable with S and R of the later work since they were modified in the arrangement of potential leads. C and K, however, are the same, and values obtained by this quarter-phase method have been included in the final adjustment given below.

3. CHANGE OF RESISTANCE METHOD

The second method for the direct measurement of inductance without recourse to computation is based upon the use of two shunts having the same inductance but different resistance. A measurement of the difference in time constant of two such shunts gives

$$\frac{L}{R_1}-\frac{L}{R_2}=\Delta T \tag{48}$$

or

$$L=\Delta T\frac{R_1R_2}{R_2-R_1} \tag{49}$$

The condition of equality of inductance can be obtained by constructing two shunts of identical dimensions, but of materials having different resistivity, or by using the same shunt at two temperatures (provided it has a high temperature coefficient of resistivity).

In the first case it is not essential that the dimensions be identical if the shape is such that the inductance can be computed, since the computed difference can be applied as a correction. That this correction does not invalidate the independence of the method is shown by the following reasoning: Let L_1 and L_2 be the true values of the inductance and L_1' and L_2' be the computed values. Substitution in (48) gives

$$\begin{aligned} T_1 &= \frac{L_1}{R_1} = \frac{\Delta T\, R_2}{R_2 - R_1(1-\nu)} \\ T_2 &= \frac{L_2}{R_2} = \frac{\Delta T\, R_1}{R_2 - R_1(1-\nu)} - \nu\,\frac{\Delta T\, R_1}{R_2 - R_1(1-\nu)} \end{aligned} \qquad (50)$$

where

$$\nu = \frac{L_1 - L_2}{L_1}$$

Now ν may be written

$$\nu = \frac{(L_1 - L_1') - (L_2 - L_2') + (L_1' - L_2')}{L_1} = \frac{\Delta_1 - \Delta_2 + \Delta_3}{L_1} \qquad (51)$$

Where Δ_3 is the computed difference and is therefore known. The terms Δ_1 and Δ_2 are the errors in the individual computed values, and it is seen that it is only their difference which enters the correction term in (51). This source of error is particularly small since the main sources of Δ_1 and Δ_2, i. e., end effects and mutual inductance in the potential circuit, would be the same in both cases.

Two such pairs of shunts were used in the present investigation, and the results of the measurements are given in Table 6. It is seen that a comparatively large difference in the computed inductance of the standards produces only a very small correction term.

TABLE 6

Results of Direct Determinations "by Construction"

Shunt	R	Comp. L	Comp. T	ν	Obs. ΔT	Obs. T	Corresponding T_s
	Ohm	Henry	Microsec.		Microsec.	Microsec.	Microsec.
E_2	0.00510	8.89×10^{-9}	1.74	0.058	8.61	1.91	10.89
F_2	.00098	9.44	9.64			10.52	
C	.000337	6.28	18.64	−0.0127	21.12	21.87	10.64
K	.01	6.36	.64			.75	
							Mean 10.77

4. HEATING METHOD

The second modification of this method, namely, using a shunt of large temperature coefficient and measuring the inductance at two temperatures, would appear to be even freer from error since there can be no question of the practical identity of the dimensions. On the other hand, even with a copper resistance it is necessary to use a considerable temperature range, and thus introduce thermal expansion and possible distortion.

The procedure which was found most satisfactory was to carry the shunt through a closed cycle of temperature over as wide a range as possible and at various points to measure, by the current-transformer method, the difference ΔT in time constant between the copper shunt and a reference shunt of manganin kept at a constant temperature. Since this method also gives the resistance of the unknown, a separate temperature or resistance measurement is not required.

At any point we have the relation

$$T_0 - T_m = \Delta T \tag{52}$$

or

$$R_0 \Delta T = L_0 - T_m R_0 \tag{53}$$

hence, if $R_0\Delta T$ is plotted against R_0, the result should be a straight line of slope T_m. Any curvature in the line is an indication of lack of constancy in L_0.

The shape which is believed to be the freest from errors due to distortion, is the inner of two concentric tubes such as was used in shunt T. It has been shown that eccentricity of the tubes does not affect the inductance and the symmetry of the arrangement would tend to produce a symmetrical temperature gradient and current distribution. Shunt *P* was constructed of this shape. Also another copper shunt *Q* of the usual bifilar strip type was built, and this heating method was used with both types. The temperature range used was from −50° C to +150° C, the lower temperatures being obtained in a bath of gasoline and CO_2 snow. The results of the measurements are given in Table 7. It is seen that the values vary considerably and much more than is indicated by the probable errors which were computed from the deviations of the individual points from the straight line for each run. This is probably due to changes in current distribution caused by local irregularities in temperature and hence resistance. This is the more surprising in that a longitudinal temperature gradient should produce no harm and the error is therefore probably due to variations over the cross section of the copper.

TABLE 7

Results of Direct Determination by Heating

Copper standard	Standard	Observed value of T_m	Equivalent value of S	Probable error	Temperature range
		Microsec.	Microsec.	Microsec.	°C
P	S	9.75	9.75	±0.16	+30−+180
P	S	10.51	10.51	.19	−70−+120
Q	S	10.53	10.53	.24	
P	R	13.56	11.51	.15	−10−+120
Q	E_2	1.37	10.35	.17	
Mean			10.53±0.20		

VI. ADJUSTMENT OF FINAL VALUE

It is evident from the results quoted above that the relative measurements can be made with much greater accuracy than the direct determinations. The adjusted results of the difference measurements were therefore taken as correct, and the true magnitude of one of the shunts was assigned from a consideration of all the direct measurements.

The shunt *S* was most centrally located in the network of differences, and all direct measurements have been referred to *S* by the corresponding differences. The values resulting from the method of direct computation are tabulated in Table 8, the weights being assigned arbitrarily after a consideration of the probable constant errors of each type and the number and self-consistency of the observations involved.

TABLE 8

Summary of Values by Computation

Standard shunt	Type	Inductance computed	Time constant computed	Corresponding T_s	Weight
		Henrys	Seconds	Seconds	
E_3	Flat strip	8.89×10^{-9}	1.74×10^{-6}	10.72×10^{-6}	8
T_2	Tube	−0.47	−0.46	10.75	8
N_1	do	−1.20	−0.61	10.87	2
A_3	Wire	247.0	+2.47	10.61	2
Sec via M	Flat strip	9.5	0.19	10.74	1
Sec via A_3	do	17.0	0.17	10.57	1
Mean				10.73 ±.05	

The quarter-phase method gave $T_c = 21.2$ and $T_k = 1.4$ microseconds; hence we get $T_S = 10.0$ and 11.3 microseconds, respectively. The results of the heating method are taken from Table 7 and those marked "construction" from Table 6. The comparison with the 1-ohm standard referred to on page — gave $T_S = 10.68$ microseconds. Assigning weights according to the self-consistency of each method, we get from Table 9 the value $T_S = 10.7$ microseconds as the most probable basis for the system. The values of the other shunts follow directly from the difference measurements and are given in Table 2.

TABLE 9

Summary of Final Values

Method	T_s	Ave. dev.	Weight
	Microsec.	Microsec.	
Computation	10.73	±0.05	20
Quarter-phase	10.6	± .5	1
Heating	10.53	± .2	1
Construction	10.77	± .09	5
1-ohm standard	10.68	± .1	5
Weighted mean	10.72	±.03	32

It is believed that these values represent the absolute time constants of the various shunts to within 0.1 or 0.2 microsecond and the relative values with rather greater precision. These standards having once been established, measurements on other shunts may be made easily by relative measurements by the current transformer or some similar method.

VII. EFFECT OF STRAY FIELDS

A factor which is often neglected in the design of shunts for use on alternating currents, but which is worthy of more attention, is the influence of stray fields. An ideal piece of apparatus should not be affected by the presence of stray electromagnetic fields, nor should it produce any field itself at outside points. In general, a design which reduces one of these effects reduces the other also; but this is not necessarily the case. The effect can be considered as a mutual inductance between the shunt and the rest of the circuit S. The error introduced into the inductance of the shunt is M_{sp}, i. e., the mutual inductance of the "potential circuit" P and the surroundings S. The effect on the surroundings, however, is M_{sc}, i. e., the mutual inductance between the "current circuit" and the surroundings. In a shunt of Type I these values coincide, but this is not the case in Type II. One great advantage of some of the tubular types of shunt is that they satisfy this ideal condition very closely.

In comparing the behavior of different shunts in this respect it is necessary to have some standard stray field as a basis of reference. I have taken for this a uniform field of intensity $H = 10I$, where I is the current in the shunt in amperes. This field is much larger than is likely to occur unintentionally in practice, but can easily be approximately realized experimentally. Since the effect depends on the direction of the field, that direction giving the maximum effect is the most definite and should be taken. In cases where the proper direction is not evident from the shape of the conductor, the maximum effect may be found as the resultant of the three components observed with fields along any three mutually perpendicular axes.

TABLE 10

Effect of Stray Fields

Shunt	Resistance	T	ΔT	$\frac{\Delta R}{R}$
	Ohm	Microsecs	Microsecs	
N_2	0.0026	....	0.9	....
T_{13}	.002	−0.5	.3	....
E_3	.005	+1.7	.8	....
L & N	.01	10.7	3.6	....
D & T	.01	9.4	1.7	$1.5 \cdot 10^{-4}$
Wolff	.01	5.5	5.2	6.6
R	.0010	12.8	11.5	13.8
GE	.001	3.5	12.7	2.3
GE compensated	.001	0.1	5.0	....

Table 10 gives a summary of the effects observed on a variety of shunts, ΔT being the change in apparent time constant due to the presence of a standard field in the most effective direction. These results indicate that the effect is comparatively small in shunts in which the potential leads are kept close together even though the working material has fairly wide spacing as in the case of the *L&N* 0.01 ohm, where the spacing is one-sixth the width of the strips. In the last three cases, however, there are fairly large loops in the potential leads and a correspondingly large error from stray fields.

In making these measurements it was noticed that in some cases the shunts showed a change of resistance when in the magnetic field. This change reversed its sign with a reversal of the field and was traced to eddy currents in the metal case surrounding the shunt. The field due to these eddy currents is nearly in quadrature with that from the main current, and the emf induced by it is, therefore, in phase with the current and produces an apparent change in resistance.

Since most shunts are arranged with metal cases to contain oil for cooling, this source of error should be carefully guarded against even in work where the phase-angle does not enter. The changes in resistance expressed as a fraction of the nominal resistance, observed with the various types when in a field of standard intensity, are given in Table 10, in the last column.

VIII. OBSERVATIONS ON VARIOUS TYPES OF SHUNT

As wide a variety as possible of the alternating-current shunts now available were compared by the current-transformer method with the standards described above. The results are given in Table 10. The values of time constant are also plotted in Fig. 11

TABLE 11

Summary of Results on Various Types of Shunts

Shunt	Resistance	Current capacity	L	T	Remarks
	Ohms	Amperes	Henrys	Microsec.	
G. E. No. 182045	0.0025	200	5.21×10^{-9}	2.08	
G. E. No. 182046	.001	500	3.46	3.46	
L & N No. 13555	.05	12	130	2.6	For comparator.
L & N No. 13582	.01	50	107	10.7	
Drysdale D	.01	100	94	9.4	
Drysdale auxiliary leads D^1	.00989	100	20.6	2.1	
Wolff No. 4361	.10		450	4.5	Return at ∞.
Wolff No. 4433	.01	50	55	5.5	Do.
Do			68	6.8	Return across top
Wolff No. 4481	.001	500	39.1	39.1	Return at ∞.
Do			35.8	35.8	Return across top
Paul No. 136	.10	15	410	4.1	

as ordinates with log $_{10}$ R as abscissae. As might be expected, shunts of the same type fall along fairly smooth curves. For comparison the values published by Orlich and Paterson and Rayner are included.

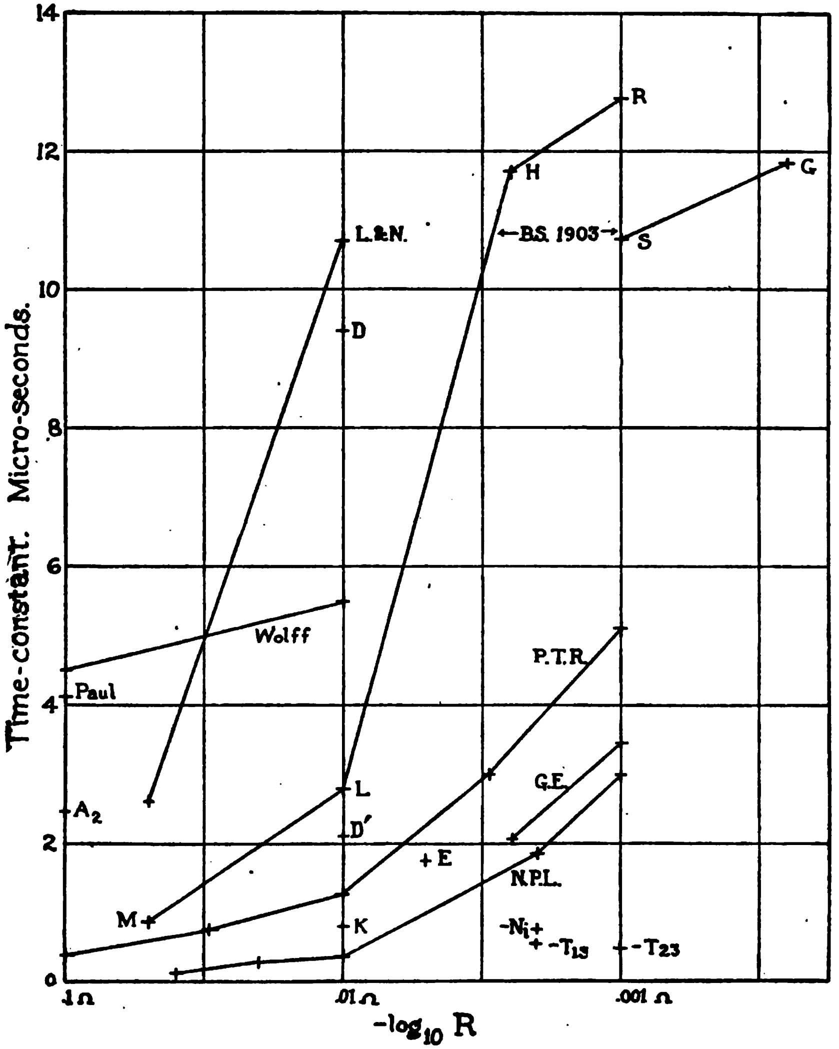


FIG. 11.—*Time constants of various types of shunts*

It is seen that in each series the time constant increases as the resistance decreases. The logical basis for the design of a series of shunts would be a constant volt drop and constant energy dissipation per unit area of cooling surface. If it is further assumed (as is approximately the case in practice) that the cross section remains geometrically similar to itself, one would expect the time constant to vary as $R^{-\frac{4}{3}}$. The curves shown, however, correspond to a variation as the −0.7 power of the resistance. This is due to the fact that in the practical designs the lower resistance shunts are worked much nearer the limit of cooling.

The point *D* corresponds to a 0.01 ohm shunt intended for alternating-current work. This is seen to have a much higher inductance than was to be expected. An investigation showed that 80 per cent of the inductance was in the copper rods leading down to the shunt proper, and point *D′* represents the result using potential leads attached directly to the resistance material.

IX. NOTES ON DESIGN

In the design of shunts for use on alternating current one must consider not only the questions of permanency and heat dissipation as in direct-current shunts, but also the additional problems of low inductance and freedom from stray fields.

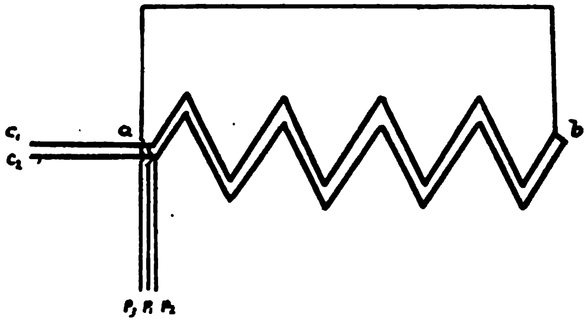


FIG. 12.—*Shunt of type I*

The problem of inductance has hitherto been attacked along two lines. In the first, as was done by Orlich,[26] Drysdale,[27] and others, the shunt is of type I, the working material is formed into a *closed* circuit of as little self-inductance as possible and the potential leads kept free from all inductive effects. In the second method, indicated by Lichtenstein [28] and definitely suggested for shunts by Campbell,[29] the potential leads are placed as close as possible to this working resistance so that the mutual inductance of the lead and the resistance is nearly equal and opposite to the self-inductance of the resistance. Figs. 12 and 13 represent schematically the two types. A notable example of the second type is the series described by Paterson and Rayner.

---

[26] Orlich, Zs. für Inst'k'de, **29**, p. 241; 1909.

[27] Drysdale, Elec'n, **66**, p. 341; 1910.

[28] Lichtenstein, Dinglers Polytchn. Jour., **321**, p. 100; 1906.

[29] Campbell, Elec'n, **61**, p. 1000; 1908.

The time constant in Fig. 12 is the same except for the effects of stray fields whether lead p_2 or p_3 is used. Now, if in Fig. 13 p_1 and p_2 are used for current terminals and c_1 and c_2 for potential terminals, the two types become identical. Now, by the reciprocal theorem[30] the inductance of the arrangement in Fig. 13 is the same whether p_1 p_2 are used as potential leads and c_1 and c_2 as current leads, or vice versa. It follows, therefore, that the inductance in either case is that of the strip *a b* with its return either at bc_2 or bp_2. Hence the advantage of the second type lies solely in the possibility of making the potential lead bp_2 thinner than the current lead bc_2. In the limiting case of zero thickness for both bp_2 and the insulation, the maximum gain is only a factor one-half.

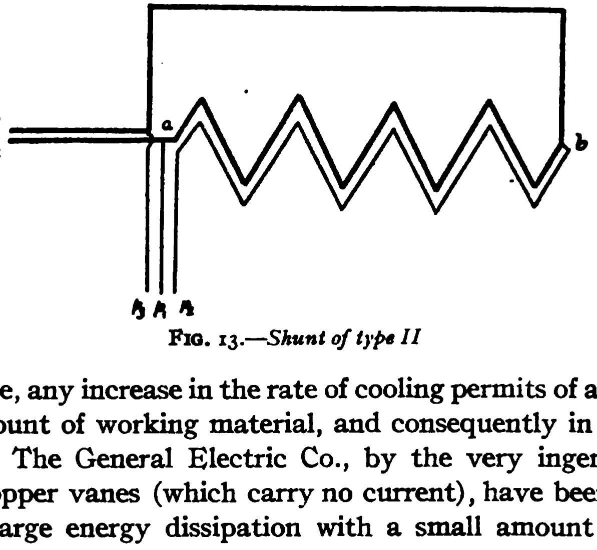


FIG. 13.—*Shunt of type II*

Of course, any increase in the rate of cooling permits of a decrease in the amount of working material, and consequently in the time constant. The General Electric Co., by the very ingenious use of large copper vanes (which carry no current), have been able to obtain a large energy dissipation with a small amount of manganin. The shunts described by Paterson and Rayner also have a very effective cooling, but in this case it has been employed to raise the permissible volt drop, and only a little of the latitude obtained by the cooling has been devoted to reducing the inductance. It is clear that with the spacing at all close either of these types practically sacrifices one-half the cooling surface of the metal. All of these types, moreover, tend to greater time constants with decreasing resistance.

Drysdale has proposed a type in which the lower resistances are built up of a number of units in parallel. With such an arrangement the phase angle would be independent of resistance. He estimates a time constant of 1.03×10^{-6} second to be easily attainable.[31] Sharp and Crawford mention a similar design, which, however, had $T = 17.10^{-6}$ second.

---

[30] Wenner, this Bulletin, 8, p. 559; 1912.

The method of attack which seems most promising to the author is to design the shunt satisfactorily from the cooling point of view and then insert in one of the potential leads sufficient mutual inductance to balance *exactly* the self-inductance of the manganin between the potential points. This can, of course, always be done by a small coil placed near the heavy-current leads. The most serious objection to this practice is the danger of stray fields, but a number of devices can be used which would render this adjusting coil nearly astatic. This method, of course, requires a measurement of the inductance, but that would be necessary anyway and with the convenience of the current-transformer method would not be a hardship.

The tubular arrangement has many advantages and permits of some rather neat schemes for adjustment. If the inner conductor be used as the working resistance and the potential leads be brought out inside the inner tube (see Fig. 9*d*) as was done with shunts T and N_i, then the mutual-inductive effects are too great and the shunt shows a negative inductance. This excess is not very large, however, and even in a 0.001-ohm standard could be neglected in almost all work.[32]

This negative excess can be reduced to any desired amount by the arrangement shown in Fig. 14 (*a*). For an exact balance the distances l and l' should be in the ratio given by—

$$\begin{aligned} l\left[\frac{a_2^2+a_1^2}{2(a_2^2-a_1^2)}-\frac{2\,a_1^2\,a_2^2}{(a_2^2-a_1^2)^2}\log\frac{a_2}{a_1}\right] = l'\Bigg[2\log\frac{a_3}{a_2}+ \\ \frac{2\,a_4^2}{a_4^2-a_3^2}\log\frac{a_4}{a_3}+\frac{2\,a_1^4}{(a_2^2-a_1^2)^2}\log\frac{a_2}{a_1}-\frac{a_2^2+a_1^2}{2(a_2^2-a_1^2)}\Bigg] \end{aligned} \qquad (54)$$

or approximately $$\frac{l}{l'} = 2+3\frac{s}{t}+6\frac{u}{t}\cdot\cdots \qquad (55)$$

where as before $s = \frac{a_4-a_3}{a_4}$, $= \frac{a_2-a_1}{a_2}$, $u = \frac{a_3-a_2}{a_3}$.

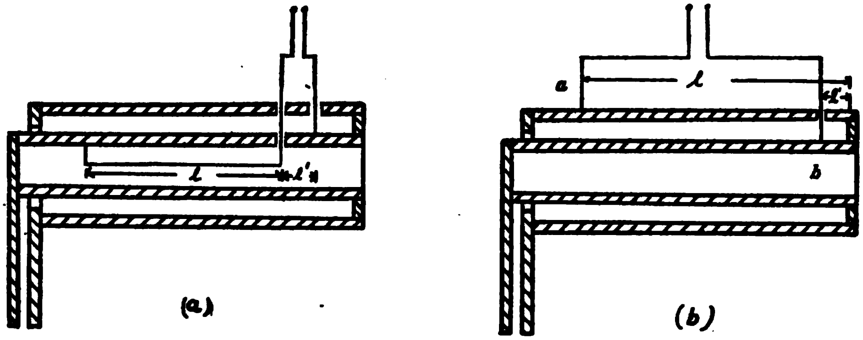
---

[31] The author regrets that he has been unable to obtain a shunt of this type to measure. The one listed in the table consisted of a single strip.

[32] Using this arrangement with one of the N. P. L. tubes would give $L = -1 \times 10^{-9}$ henry instead of $+3 \times 10^{-9}$ henry as now arranged.

Another interesting combination is that shown in Fig. 14 (*b*). Here (with suitable ratios of *l* to *l'*) we have a shunt having zero phase angle, and also no emf induced in the potential leads. In other words, the negative inductance of the outer tube with return inside is balanced by the positive inductance of the shorter length of inner tube so that the difference in potential between the points *a* and *b* is in phase with the total current. If the inductance of the disk is neglected, the ratio should be

$$\frac{l}{l'} = 3 + 2\frac{t}{s} + 6\frac{u}{s} \text{ (approx.)} \tag{56}$$



(*a*) (*b*)

FIG. 14.—*Tubular shunts with compensating potential leads*

X. MUTUAL INDUCTANCES

A mutual inductance has usually been regarded as yielding a secondary emf in exact quadrature with the primary current, though occasionally the necessity of using stranded wire in the windings has been pointed out. In case the primary is to carry a heavy current the departure from quadrature may become very considerable. Using as primary a copper strip 5 cm by 0.32 cm two secondary coils showed voltages having a phase difference of 75 minutes at 60 cycles per second. With due care, however, the phase defect of a mutual inductance may be made much smaller than that of a shunt of the same current capacity, so that the mutual inductance and quarter-phase methods, described above, are most useful in measuring the shunts, rather than in using the shunts to measure the mutual inductances.

The factors which produce this shift of phase can be seen by working out in detail the case where the primary and secondary windings each consist of two thin wires in parallel as indicated in

Fig. 15. Applying Kirchoff's laws to these four circuits, we get for the relation between secondary voltage and primary current

$$E_s = I_p\,(R + j\,\omega\,M) \tag{57}$$

$$\text{where } M = M_{24} + \frac{1}{R_s\,R_p}\Big[M_{13}R_2R_4 + M_{14}R_2R_3 + M_{23}R_1R_4 - M_{24}(R_2R_4 + R_2R_3 + R_1R_4)\Big] \tag{58}$$

$$\text{and} \qquad R = \frac{\omega^2 R_1R_2R_3R_4}{R_pR_s}\left\{\frac{1}{R_s}\left(\frac{L_4'}{R_4} - \frac{L_3'}{R_3}\right)\left(\frac{A}{R_1} + \frac{B}{R_2}\right) + \frac{1}{R_p}\left(\frac{L_2'}{R_2} - \frac{L_1'}{R_1}\right)\left(\frac{C}{R_s} + \frac{D}{R_4}\right)\right\} \tag{59}$$

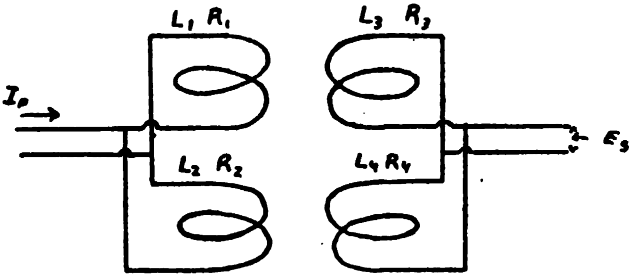


Fig. 15.—*Four-coil model of impure mutual inductance*

In these equations R_1 and L_1 are the resistance and inductance of the circuit 1, R_2 and L_2 of circuit 2, etc., and M_{12} is the mutual inductance between circuits 1 and 2, etc.

Also $L'_1 = L_1 - M_{12}$, $L_2' = L_2 - M_{12}$, $L_3' = L_3 - M_{34}$, $L'_4 = L_4 - M_{34}$

$$R_p = R_1 + R_2,\ R_s = R_3 + R_4$$

and

$$A = M_{13} - M_{14}$$
$$B = M_{23} - M_{24}$$
$$C = M_{13} - M_{23}$$
$$D = M_{14} - M_{24}$$

In deriving these equations terms of higher order in $\frac{\omega L}{R}$ and $\frac{\omega M}{R}$ have been neglected. An inspection of (59) shows that this resistance term is in two parts, the first of which may be considered as due to the secondary circuit, while the second term in the brackets is due to the primary circuit. This can be seen most clearly by letting one (say, the secondary) circuit become linear, i. e., let 3 and 4 coincide. Then the first term vanishes but the second term remains and is a function of the dimensions and relative position of the parts of the primary circuits. For brevity these terms will be referred to as the "secondary impurity" and "primary impurity," respectively.

It will also be noticed that each of these terms contains two factors. The first $\frac{L'_2}{R_2}-\frac{L'_1}{R_1}$ is proportional to the difference in phase of the two parts of the primary current. The second involves $(M_{13}-M_{23})$ and $(M_{14}-M_{24})$, that is, the difference in the mutual inductance of various parts of the primary on a single part of the secondary. If either factor vanishes, then the whole term will vanish regardless of the other factor.

The deduction of the equation (59) may be generalized to cover any number of elementary filaments and thus to represent a filamentary flow in a solid conductor. In case the secondary is linear the primary impurity becomes proportional to

$$\sum_{k=1}^{k=n} \Delta\theta_k \, \Delta m_k \qquad (60)$$

Where $\Delta\theta_k$ is the difference in phase angle between the current in the *k*th filament and the total current and Δm_k is the difference between the mutual inductance of the *k*th filament on the secondary and the average mutual inductance. The expression for the secondary impurity is of course similar.

The usual method of stranding tends to reduce both factors in these errors, but becomes very laborious if the coil is to carry heavy currents. *A* and *B* of (59) become zero, regardless of the thickness of the secondary wire if the magnetic field of the primary is so localized that there is no magnetic field at points where the secondary copper is placed. Conversely *C* and *D* will vanish if a current in the secondary produces no magnetic field where the primary copper is located. The required localization of the magnetic field to make either pair zero is easily obtained by using one winding in the form of a uniformly wound toroid, or a long straight solenoid (which is really a special case of the former). It is, however, impossible to make both errors zero by this arrangement, since if both circuits are closed toroids they either have no flux in common or one is within the other and its copper is in the field of the other.

The logical way to construct a pure mutual inductance is, therefore, to eliminate one source of impurity by making *A* and *B* zero and to minimize the other by making the time constant of the various elementary filaments as nearly equal as possible. This means making one coil in the form of a uniformly wound toroid and then stranding this coil. To be efficient the strands should, of course, be thoroughly intermixed. With such a construction the character of the other coil is immaterial. It is therefore preferable to use the toroidal coil as secondary, since one can then use as heavy copper as desired in the primary. A coil of this type used in this work showed no detectible primary impurity, though the primary winding was of 130 000 circular mil cable.

Equation (60) forms the basis of a method of testing inductances having stranded primary windings. Consider a coil having a linear secondary and the primary wound from a number of parallel strands with a small coil c_1, c_2 ... in series with each strand. Using each strand separately as a primary, the mutual inductance between it and the secondary can be measured. Subtracting each of these values from the average of all gives the successive values of Δm_κ. Now, passing the full primary current through all the strands in parallel the relative phases of the components are to be determined. This can be done by placing a small exploring coil near each of the coils, c_1, c_2 ... and observing the phase of the induced emf relative to any fixed standard. The differences of these values from their mean give the values of $\Delta\theta_\kappa$. The summation of (60) may thus be directly observed and gives the amount by which the primary impurity differs from that due to a single strand. This method was used in one of the mutual inductances used in the resistance measurements where there were 12 strands and was found very convenient.

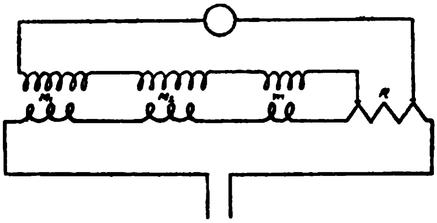


FIG. 16.—*Connection for comparing the phase defects of mutual inductances*

What is perhaps the simplest method of comparing the phase defects of mutual inductances of nearly equal magnitude is indicated in Fig. 16. The two inductances to be compared are connected with their primaries in series with the primary of a small variable mutual inductance m and with a very low resistance R. This latter may well be arranged as in Fig. 6. The secondaries of M_1 and M_2 are connected in opposition and any difference in voltage is balanced by m and R. At a balance the algebraic sum of the three mutual inductances and also of the four four-terminal "resistances" (as defined by equation 9, page 381) must be zero. By a little ingenuity in connecting coils in series, it is possible to intercompare mutual inductances of widely different values without ever using a very large variable inductance at *m*. The "resistance" of *m* may therefore be kept negligible.

While the primary error is the more dangerous, the secondary error may not be negligible. A number of measurements were made on circuits in which the primary error had been eliminated by using a toroidal or solenoidal secondary. These comparisons brought out some interesting facts about this secondary error.

TABLE 15

Results of Measurements on Secondary Impurity of Mutual Inductances

Coil	M	Radius of coil—r	Radius of wire—a	Turns per centimeter n	a^4n^3r	T	$\frac{R}{f^2}$	Remarks
	Microhenrys	cm	cm		cm^2	Microseconds	Ohms per cycle^2	
p.......	4.40	1.32	0.020	7.5	$0.14.10^{-4}$	0.03	$+6.\times10^{-12}$	Solenoid.
l.......	.47	.60	.040	4.2	.27	.39	+7.0	Do.
m......	6.00	1.05	.020	16.0	.54	.00	−0.0	Do.
la......	4.89	1.14	.032	8.1	.75	.04	+8.0	Toroid.
0.......	1.18	.60	.040	9.5	1.41	.23	11.0	Solenoid.
5g_1.....	3.23	*2.64×3.00	.040	7.79	2.23	.14	18.0	Toroid.
h_1......	5.25	1.25	.040	9.5	2.90	.10	20.0	Solenoid.
n.......	2,90	1.07	.051	7.5	4.03	.34	39.0	Do.
f.......	4.89	1.38	.051	7.3	4.98	.22	43.0	Do.
q.......	3.50	1.39	†7×0.01	5.2	....	.06	8.0	Litzen-draht 5×7 No. 35 B. & S.
h_2......	5.97	1,33	.040	9.5	3.09	.29	69.0	Outside h_1.
h_3......	6.73	1.43	.040	9.5	3.30	.43	115.0	Outside h_2.
h_4......	7.58	1.51	.040	9.5	3.48	.61	182.0	Outside h_3.
h_5......	8.38	1.60	.040	9.5	3.69	.73	242.0	Outside h_4.
5g_2.....	3.66	*2.87×3.27	.040	7.58	2.59	.20	29.0	Toroid. Outside g_1.

*Coils g_1 and g_2 were of rectangular section and of the dimensions indicated.

† Each coil *q* consisted of one of the five seven-wire strands,

The group of 15 coils compared in this manner are listed in Table 15. The complete mathematical calculation of the error due to eddy currents in the secondary would be extremely difficult, even in the simplest case of a long straight uniform solenoid. A rough approximation may be obtained for this case by assuming the actual secondary wire replaced by two thin filaments parallel to the axis of the wire and at a distance apart $2y$ in the direction of the radius of the coil. It may also be assumed that the ordinary two-terminal resistance of each filament is equal to twice the resistance of the complete wire. The various quantities entering equation (59) may then be computed and it appears that the "resistance" is given by

$$R = K\omega^2 a^2 n^2 y^2 r \tag{61}$$

where

$\omega = 2\pi \times$ frequency, a = radius of wire.
n = turns per centimeter of winding, r = radius of coil.
In case y may be taken a constant fraction of a as would appear reasonable if r is large, we have

$$R = K'\omega^2 a^4 n^2 r \tag{62}$$

This is in agreement with dimensional reasoning, which shows that R must be reducible to the form

$$R = \omega a \psi \left[\frac{\omega a^2}{\rho}, \; an \; , \frac{a}{r} \right] \tag{63}$$

where ρ is the resistivity of the material and ψ an unknown function.

The observed differences of $\frac{R}{f^2}$ for the various coils from an arbitrary zero have been plotted in Fig. 17 (*I*) against the quantity a^4n^2r. According to (62) this should yield a straight line. The points seem to indicate a slight curvature, but the agreement is within the precision needed in the work on shunts. An extrapolation of the line to the axis where $a^4n^2r = o$ gives the true zero for the system. It may be noted that points corresponding to the closed toroids $5g_1$ and $1a$ fall along the same line as those for the long straight solenoids.

In coils of more than one layer, the outer layers show an abnormally great secondary error. This is shown in Fig. 17 (*II*), where the time constants of five coils wound one above the other are plotted against the values of a^4n^2r. The innermost coil is seen to be normal, while the outer coils have a greatly increased phase defect. This effect is due to the fact that the eddy currents in the inner wires produce a magnetic field in quadrature with the main field. This field is linked with all the coils outside of it and induces a large out-of-phase emf in them, but does not link the coils inside of it. This shows the danger of using multiple layer coils for work of this character.

A further source of secondary impurity is the capacity of the windings. If a condenser of capacity C is connected across the terminals of a secondary winding of resistance R, then the mutual inductance will show an apparent phase defect of

$$\tau = \omega c R \tag{64}$$

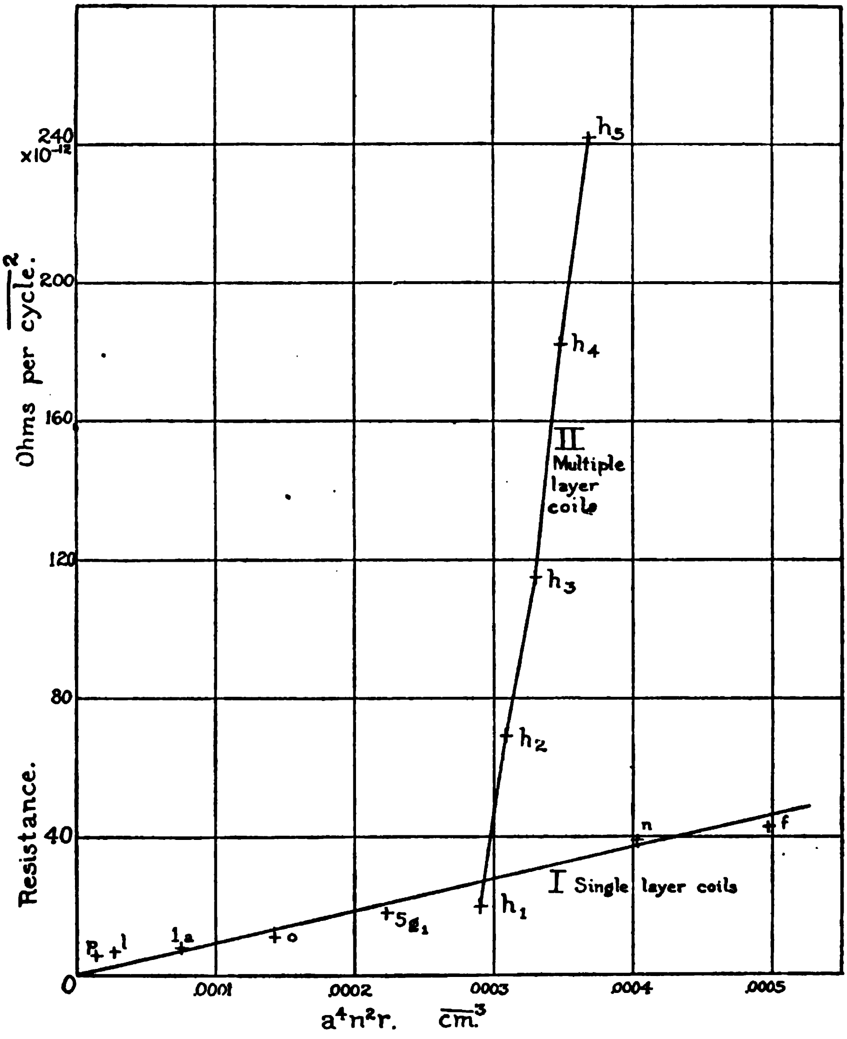


FIG. 17.—*Secondary impurity of mutual inductances*

This effect is entirely negligible in coils of the range used, say $M = 10^{-5}$ henry, but may become very serious when the resistance of the windings becomes large. In comparing the phase angles of mutual inductances, this effect of capacity is useful, since by connecting a microfarad across one of the coils, its emf is made to lag more than before, and by noting the direction of the change in the resistance setting, it is readily seen which coil has the greater phase angle.

XI. SUMMARY

The results of this study of four-terminal impedances are summarized below. The discussion of the inductance of shunts has been clarified by the classification of such apparatus into two main types and also by the use of the idea of the inductance of an open circuit "with a definite return." The close analogy between shunts and mutual inductances has been pointed out. The causes of phase defects in mutual inductances have been pointed out, and methods of avoiding or minimizing these sources of error suggested. The secondary impurity has been investigated and the abnormal increase of this error in multiple layer coils noted.

On the more practical side two relative methods for the comparison of the time constants of shunts have been studied and the sources of error determined. One of these has been shown to be very simple, accurate, and easily set up. Three possible types of shunts whose inductance can be computed from the dimensions have been studied, and the sources of error shown to be much smaller than would be expected. The formulæ for various arrangements of tubular shunts have been deduced from a new point of view, and have been put in a simplified form for computation. Two direct methods for the measurement of inductance have been tried and found to agree with the values found by computation. These methods were, however, less satisfactory than direct computation. The time constants of a number of shunts at the Bureau of Standards and Harvard University have been determined to within one or two tenths of a microsecond. These may now be used as standards for the calibration of other shunts. The inductance and susceptibility to stray fields of a number of commercial types of shunt have been measured. In some cases a change of resistance in the presence of the external field has been detected.

WASHINGTON, December 30, 1915.

NOTATION

A, B, C, D	Differences in mutual inductance.
a, a_1, a_2	Radii of wires or tubes.
b, c	Thickness of strips.
d, d_{11}	Distance c. to c. of wires, strips, or filaments.
D_{11}, D_{12}	Geometric mean distances.
E	Maximum voltage.
e	Instantaneous voltage.
f	Frequency.
g	Thickness of insulation between strips.
H	Magnetic field intensity.
I_m, i	Maximum and instantaneous currents.
i_1, i_0	Instantaneous current densities.
j	$\sqrt{-1}$.
K	Undetermined constant.
L	Inductance.
l	Length of circuits.
M, m	Mutual inductances.
n	Pitch of winding.
P	Ratio of current transformer.
R	Resistance.
r	Radius of coil.
s, t, u	Shape ratios of tubes.
S_1, S_2	Cross-sectional areas of conductors.
t	Time.
T	Time constant.
w	Width of strip.
x	Distance from axis to filament considered.
y	Distance from axis to equivalent filament.
$\alpha, \beta, \gamma, \delta, \eta, \kappa, \lambda, \varsigma$	Shape ratios of strip shunts.
θ	Phase angle of shunt.
μ	Apparent phase angle of transformer.
ν	Correction term.
ρ	Resistivity.
τ	Phase defect of a mutual inductance.
ϕ	Flux per unit length of circuit.
φ	True angle of transformer.
ω	$2\pi \times$ frequency.

SENSITIVITY AND MAGNETIC SHIELDING TESTS OF A THOMSON GALVANOMETER FOR USE IN RADIOMETRY

By W. W. Coblentz

CONTENTS

Page
I. Introduction 423
II. Experimental tests of galvanometer coils 424
  1. The form of the coil 424
  2. The standard coils 426
  3. Method of comparison of various coils 428
  4. Discussion of the results of tests on various coils 428
III. Comparison of astatic magnet systems 431
IV. Test of shielding against magnetic disturbances 432
V. Test of a vacuum galvanometer 438
VI. Summary 443
Appendix.—Note I. Mounting for vacuum thermopiles 444

I. INTRODUCTION

In attempting a further improvement in stellar radiometry[1] it was deemed desirable to inquire first into the construction of the galvanometer which is one of the three important elements in the radiometric apparatus, the other two elements being the thermocouple and the reflecting mirror. As indicated in the previous paper, a further improvement in the stellar thermocouple will depend more upon the nicety of construction than upon the emf of the thermoelement. New alloys having a high thermal emf and a high tensile strength must, of course, be sought. However, if the thickness of the material can not be reduced to smaller dimensions than those already employed, then the prospects for greatly increasing the sensitivity of the thermocouple are not very encouraging.

A further increase in the galvonometer sensitivity must evidently be sought through further improvements in the coils and especially in the suspended magnet system. In spite of all that has been written upon the construction of galvanometer coils, wound in sections of graded wire, there seemed to be no data at hand showing the behavior of the different sections as compared with what was to be expected from theory. In fact, part of the present investigation is the result of a disagreement between the observed and the theoretical performmance of the different sections of several galvanometer coils which had been subjected to test. This paper gives the results of experiments (1) on galvanometer coils of various designs, (2) on various magnet systems, (3) on shielding the galvanometer from magnetic disturbances, and (4) on vacuum galvanometers.

---

[1] This Bulletin, 11, p. 613; 1915.

The increase in sensitivity as a result of placing the magnet system in an evacuated inclosure has already been discussed,[2] and more precise data are given in the present paper. In the previous tests the instrument could not be shielded from magnetic disturbances. In the vacuum galvanometer, as it will be used in practice, one of the inner shields is to be provided with a cover, so that it can be utilized as an inclosure which may be evacuated. The sensitivity attainable will depend upon the weight and upon the period that can be given to the suspended magnet system. This will, of course, depend upon the environment in which the instrument will be used. From the performance of the instrument when shielded, as described on a subsequent page, it appears that magnetic disturbances can be reduced to a very small value. It is to be emphasized, however, that with such a highly shielded galvanometer it is difficult to maintain a long period because of the necessity of using powerful control magnets which must be placed close to the galvanometer. These control magnets are so close that any slight change in their position, or in the magnetic force exerted by them, easily affects the astaticism of the needle.

II. EXPERIMENTAL TESTS OF GALVANOMETER COILS

1. THE FORM OF THE COIL

This subject has received so much discussion that there seems to be little need for further remarks. Maxwell has shown that each layer of spires should lie within the surface having the polar equation $r^2 = d^2 \sin \theta$, where r is the length of the radius (the distance from the magnet of infinitesimal length) making an angle θ with the axis of the coil, and d the value of r when $\theta = 90°$. Freudenberger[3] has used the formula $r = p \sin {}^2\theta$, which produces a thinner coil than obtained by using the original formula. He was interested in a coil having a resistance of about 100 ohms and found that a coil made of No. 36 B. & S. wire was as good as one made of wires of different diameters. In fact, he mentions that coils might be wound to the resistance desired, using No. 36 wire.

---

[2] This Bulletin, 11, p. 177; 1914.

[3] Freudenberger, Elect. World, Sept. 29; 1906.

It has been shown [4] that if the space in which the needle hangs is not made cylindrical, the shape of it is of some importance, as it is possible to place spires in positions in which they produce a magnetic effect which is opposed to that of the complete coil.

Abbot [5] has made theoretical computations of the force exerted by coils wound in three sections, of equal resistance of graded wire. The data published give the force exerted by each section of the coil.

No experimental tests having been published, the writer made tests of the force exerted by each of the three sections of a 20-ohm coil (the 21.1-ohm coil in Table I), which had been wound according to theoretical specifications to give the maximum total force. The theoretical data indicated that the force exerted should be closely the same for each section of this particular type of coil. However, as a general rule, this is not necessary in order to obtain a coil that exerts the maximum total force. The results of this test (see Table I) showed that experimentally (owing to difficulties in winding the coils) the force exerted by each section of the 20-ohm coil is not the same as was to be expected from theoretical considerations, and that the outer section exerted the greatest force. In other words, the outer section is the most efficient of the three components of this 20-ohm coil. The inner section was found to be the least efficient, and in view of the fact that a galvanometer was desired which had a lower resistance than was obtainable with these 20-ohm coils joined in parallel, it was deemed desirable to determine whether (without making a prolonged investigation) an efficient coil could be found by trial, which had the properties of the central and outer sections of the 20-ohm coil. As is well known and as was mentioned in a previous paper,[6] owing to the difficulties in winding fine wires and owing to the large amount of space occupied by the insulation when using fine wires, a more sensitive 4-ohm coil galvanometer is to be expected to result from constructing the coils of heavy wires (hence of low resistance, say 2.5 ohms) which are joined in series than is to be expected to result from coils of the same size which are wound with fine wire (hence of high resistance, say 10 ohms) which are joined in series parallel. However, as will be shown presently, these two kinds of coils differed but little in the force exerted, although the wires had been selected to give closely the same sized coils. In previous tests no marked difference was found in galvanometers having 20-ohm coils wound in three and in five sections of graded wire. The records of the performance of 12 galvanometers indicate (as mentioned in the paper just quoted) that the greatest advances in increasing the sensitivity of the galvanometer are to be expected from improvements in the suspended system.

---

[4] Ayrton, Mather, and Sumpner, Phil. Mag., **30**, p. 58; 1890.

[5] Abbot, Astrophys. Jour., **18**, p. 1, 1903; Ann. Astrophys. Obs., **1**, p. 250, 1902.

[6] This Bulletin, **11**, pp. 180–181. (See Fig. 9.)

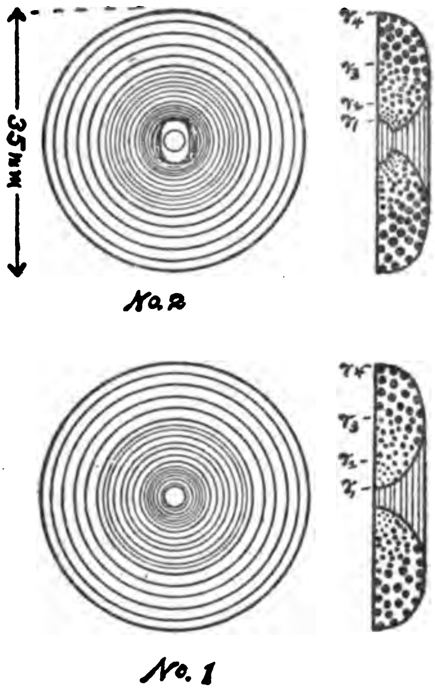


Fig. 1.—*Form of the coil when using different mandrels*

The mandrels used in winding the coils were of two types, producing coils of the form shown in Fig. 1, which shows a compound coil wound in three sections of graded wire. Mandrel No. 2 was tried to determine whether a marked improvement would result in the magnetic field near the galvanometer needles. When using fine wires for the inner section of the coil, this form of winding (mandrel No. 2) was found to be detrimental.

In the coils to be described presently the insulation was a single layer of silk, excepting in the 0.6-ohm coil, which was covered with a double layer of silk. The thickness of the insulation was about 0.043 mm, which is practically the same as used by Abbot (loc. cit.). The thickness of the various samples of wire, some of which had been purchased (from A. F. Moore, Philadelphia) eight years ago, varied from 0.001 to 0.002 mm.

2. THE STANDARD COILS

All the coils investigated were compared with a set of three coils, which was used as a standard. These three coils were mounted securely in an ironclad support, two in the lower part

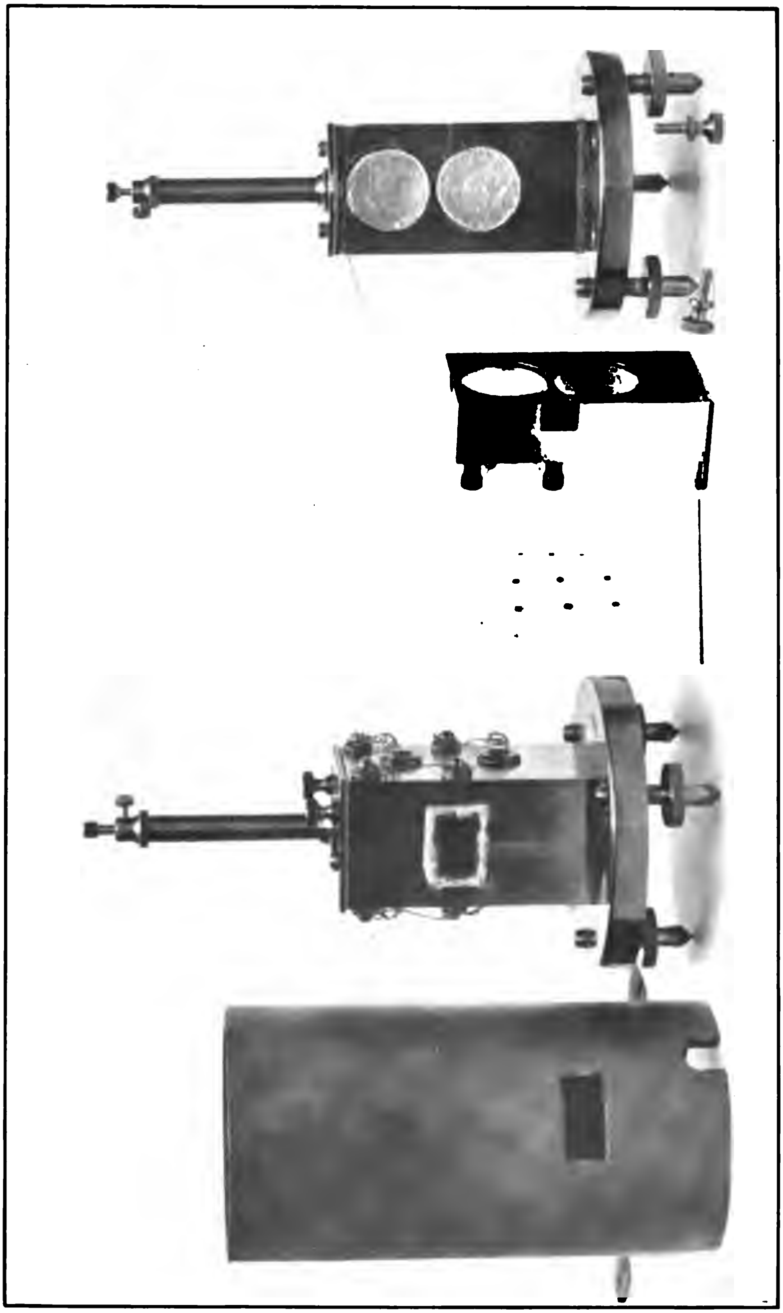


FIG. 2.—*Iron-clad galvanometers showing the coils embedded in Swedish iron; also the suspended systems of magnets (center of photograph) and the "inner shield" of transformer iron*

and one in the upper position, as shown in Fig. 2. The coil which was to be compared was mounted at a fixed distance opposite the upper standard coil. The object of the three standard coils was to enable one to test the symmetry of the deflections of the suspended magnet system, which might be affected in mounting the various coils which were being tested. Lead wires from each coil, or sections of a coil, were connected with small mercury cups in a block of paraffin. By this means it was possible to send an electric current through any coil in the instrument. After mounting a coil for comparison the iron shields were put in place and the magnet system was astatized to give a single swing of two to three seconds. The symmetry of the deflections produced by the three standard coils was not affected by slight changes in level. It was therefore assumed that the coils under examination were being intercompared with considerable accuracy.

The details of construction of the standard coils are given in Table 1. Each coil was wound in two sections and had a resistance of 10.2 ohms. The form of the coil is shown in No. 2 of Fig. 1. As shown in Table 1, another 10-ohm coil wound, with three kinds of wire, on mandrel No. 1, Fig. 1, is 17 per cent more efficient than the one which happened to be used as a standard.

TABLE 1

Efficiency of Coils of Various Design as Compared with a Set of Standard Coils

Specifications of coils												Force exerted				Efficiency as compared with standard	
Resistance	Kind of wire			Radii of sections				Resistance of sections			Mandrel	By each section			Ratio; standard test	Test coils in series	Test coils in series parallel
	r_1	r_2	r_3	r_1	r_2	r_3	r_4	1	2	3		1	2	3			
ohms					mm				ohms								
0.62	No. 22					17.0				0.62	2				4.0:1	1.00	
2.26	28	24		5.0	9.5	16.5		1.20		1.06	2	1.0	1.11		1.79:1	1.18	1.18
2.43	28	24		1.5	9.0	17.0		1.30		1.13	1	1.0	0.83		1.73:1	1.18	1.18
3.17	28	26		5.0	8.5	16.5		1.07		2.10	2	1.0	1.3		1.95:1		.92
6.3	28			2.5		15.5				6.3	1				1.10:1		
8.6	32	28		2.5	7.0	16.0		2.2		6.4	1	1.0	1.88		0.946:1		1.17
10.2	34	28		4.0	6.0	15.5		3.16		7.04	2	1.0	3.66		Standard coil		
10.5	34	30	28	2.0	4.3	8.5	14.2	3.1	3.6	3.8	1	1.0	1.1	1.05	0.856:1		1.17
11.1	30	28		5.0	10.0	17.0		4.2		6.9	2	1.0	1.26		0.922:1		
20.8	40	36	32	1.2	3.2	5.0	9.5				1				0.78:1		
21.0	38	34	28								1	1.0	1.18	1.26			
21.1	38	34	28	1.5	4.5	7.5	16.5	6.7	7.0	6.8	1	1.0	1.40	1.83	0.622:1		

3. METHOD OF COMPARISON OF VARIOUS COILS

The behavior of the coil under test was determined by observing the deflection produced by a given current as compared with the deflection produced by the same current when passed through the standard coils. From tests made at various times throughout this investigation it was found that each one of the three standard coils produced the same deflections. The upper standard coil was therefore used in making the comparison. In Table 1 column 6 is given the force exerted by different sections of a coil, the inner section, "No. 1," of each coil being used as a standard of reference. Column 7 gives the force exerted by the upper standard coil as compared with the coil under test. This of course is merely an intermediate step, for the comparison must be made with galvanometer coils having the same resistance. Columns 8 and 9 give the desired data, which will be discussed on a subsequent page. It will be sufficient to add that by efficiency is meant the ratio of the force exerted by the test coil as compared with the standard coil (of 10.2 ohms) when used under comparable conditions. For example, the 0.62-ohm coils would be joined all in series, giving a galvanometer resistance of 2.48 ohms, while the standard 10.2-ohm coils would be joined all in parallel, giving a resistance of 2.55 ohms.

In the thermopiles described in previous papers the elements were joined either all in series, producing a resistance of about 9 ohms, or joined two in series parallel, producing a resistance of about 2 ohms. Table 1 therefore gives the way in which the above coils would be used in connection with these thermopiles. The efficiency of each coil is of course the same in whatever manner it may be connected. In reducing this data, the force exerted by the coil is assumed to be proportional to the square root of its resistance. This, however, is of minor importance in view of the fact that comparison is made only of coils having closely the same resistance.

4. DISCUSSION OF THE RESULTS OF TESTS ON VARIOUS COILS

The results obtained on the different coils are summarized in Table 1. As already mentioned, the 10-ohm coils used as standards of comparison happened to be less efficient than some of the coils under investigation. From Table 1 it may be noticed that a 10.5-ohm coil made of three sizes of wire (American gauge Nos. 34, 30, and 28), an 8.6-ohm coil made of two sizes of wire (Nos. 32 and 28), and a 2.4-ohm coil made of two sizes of wire (Nos. 28

and 24), all of which were practically the same in size, exert the same force, which is about 18 per cent greater than the standard. In the test on the 2.26-ohm coil both types of mandrels (Fig. 1) were used in order to determine whether in using Nos. 28 and 24 wire, a greater efficiency would result from placing the wires nearer the center of the coil. (See test of a 2.43-ohm coil, mandrel No. 1.) As shown in Table 1 (force exerted), these two coils differ by only 3 per cent (1.79:1.73) in the force they exerted. It is of interest to note that in the 2.26-ohm coil the outer section exerts a force which is 11 per cent greater than that exerted by the inner section, while in the 2.43-ohm coil the inner coil exerts the greater force. The latter coil is the more efficient, showing that although the spires are nearer the magnets they do not occupy positions in which they produce a magnetic effect which is opposed to that of the complete coil.[7] The efficiency of these types of coils (2.4, 8.6, and 10.5 ohms, respectively) being so closely the same there is no choice in their use with an external resistance of 2 or 8 ohms. As mentioned elsewhere,[8] a galvanometer, in which the coils have a resistance of 8 ohms, is the most suitable to be used with bismuth-silver (or copper) thermopiles which have a resistance of about 8 ohms, when all the elements are joined in series, and a resistance of 2 ohms when the elements are connected in series parallel. Comparing the 8.6-ohm coils joined in series parallel with the 2.26-ohm coils connected all in series, it was found that the latter arrangement was about 2 per cent more efficient than the 8.6-ohm coils.

The performance of the 6.3-ohm coil is of interest in view of the fact that it was made of a single size (No. 28) wire, to utilize the best part of the 21.1-ohm coil previously mentioned. It produced a deflection of 2.67 cm; and under the same conditions the 21.1-ohm coil, of graded wire, gave a deflection of 5.07 cm. When used with an external resistance of about 6 ohms, the above 6.3-ohm coils would be joined in series parallel, thus producing a deflection of 5.34 cm. Similarly, the four 21.1-ohm coils would all be joined in parallel, having a resistance of 5.3 ohms and producing a deflection of 5.07 cm; or 5.53 cm on the basis of equal resistance. There is therefore but little difference (only 4 per cent) in the efficiency of these two coils. Of course, a 6-ohm coil of graded wire may perhaps be found which exerts a greater force than this coil which was made of a single size of wire. However, the gain in the force exerted by the 6-ohm coil of graded wire can not be expected to be very great in view of the fact that, theoretically, a 4-coil galvanometer of 6-ohm coils joined in series parallel is no more efficient than a galvanometer of 24-ohm coils joined all in parallel, and in view of the fact that in practice the low-resistance coils joined in series were found to be but little more efficient than coils of four times this resistance, which were joined all in parallel. Other facts must also be considered; for example, the range of proportionality of deflection with current may be small for the 6-ohm coil of single wire, while it is known to hold over a wide range (20 cm deflection, scale at 1 m) in the 21.1-ohm coil.

---

[7] Ayrton, Mather, and Sumpner, Phil. Mag., 30, p. 58; 1890.

[8] This Bulletin, 11, p. 132; 1914.

The data on the 21-ohm coils are of interest in view of the fact that this type of coil has been extensively used, being wound to fit closely the theoretical specifications. The coil is in three sections of Nos. 38, 34, and 28 wire. One peculiarity in this type of coil is that the force exerted by the inner section is from 50 to 60 per cent less than that exerted by the outer section, although the force exerted was supposed to be closely the same for each section. Another coil of this type gave similar results. That this is not due to the fact that the coils were imbedded in Swedish iron was proven by repeating the test on coils mounted in a brass support. The explanation is no doubt to be found in the fact that when using the finest wire with its disproportionately thick insulation as compared with a heavy wire, the resistance per turn of wire increases much more rapidly than obtains in the heavier wire. The outer section contains more than 15 times the length of wire, for the same resistance, and, as is well known, after passing out a certain distance from the center of the coil, the force exerted by each turn decreases but little with increase in diameter. All the coils just described are from 31 to 34 mm in diameter.

The 20.8-ohm coil (Table 1) is one of the earliest designs worked with by the writer.[9] This coil has a rather small diameter and its performance is poor. The proportionality of deflection to current does not obtain for deflections greater than 6 to 7 cm. This coil gave a deflection of 4.05 cm under the same conditions as obtained in the test of the 21.1-ohm coil (33 mm diameter) which gave a deflection of 5.15 cm. In other words, the 21.1-ohm coil was 27 per cent more efficient than the smaller sized coil having the same resistance. This had already been found from tests on a complete galvanometer containing the small coils and a more suitable magnet system as compared with the 21.1-ohm coils (Fig. 2, the opened galvanometer to the right in this photograph) which were used with the vacuum thermocouples used in measuring the radiation from stars. The foregoing data are necessarily of a preliminary nature in view of the numerous factors which enter into the design of efficient galvanometer coils. The chief aim in the present communication is to call attention to the disagreement between certain theoretical specifications and the results obtained by experiment, which emphasizes the importance of further investigations.

---

[9] This Bulletin, 4, p. 392, 1908; Mendenhall and Waidner, Amer. Jour. Sci. (4), 12, p. 249, 1901.

III. COMPARISON OF ASTATIC MAGNET SYSTEMS

Various experimenters have made tests on the lengths of the magnets to be used in a galvanometer suspension, and the conclusion arrived at is that the magnets should be from 1.5 to 2 mm in length. The tests from which these conclusions were drawn were made on single magnets. In view of the fact that the size of the mirror is a very important factor in determining the sensitivity, it was deemed of importance to make tests on complate magnet systems in which the mirrors were of the same size and thickness[10] and only the lengths of the magnets were varied. Each system consisted of two groups of magnets (tungsten steel "glass hard" magnetized in a ⊏ ⊐ shaped device after mounting), four magnets in each group, the width of each magnet being about 0.25 mm and the thickness being about 0.1 mm.

In one system (Fig. 3, ◬ ◬ ◬), the magnets were 2 mm long; in the other system the magnets were 4 mm long. (Fig. 3, × × ×), and the latter gave only about two-thirds the deflection of the former for the same stimulus. In this test the mirrors were 2.0 by 2.8 mm. In another suspension having needles 2.2 mm long and having mirror 3 mm diameter the sensitivity (Fig. 3, ⊙ ⊙ ⊙) is the same as for the long needles. In other words, the large mirror reduces the sensitivity by about 30 per cent.

In another suspended system of magnets a decrease in sensitivity of over 20 per cent was introduced by substituting a mirror 2.5 mm in diameter for one which was 1.5 by 2.5 mm. In the latter the longer edge was, of course, placed vertically in order to reduce the inertia.

In Fig. 2 are shown several astatic magnet systems. The largest one contains eight magnets (in two groups) each one of which is 2 mm in length. The mirror is rotated 90° from its true position to show its size. The distance between the two sets of magnets is 35 mm. The next to the largest magnet system belongs to the galvanometer to the right in the photograph. It was used in measuring the heat from stars. The smallest magnetic system (magnets 1 mm long) was used with the 20.8-ohm coils (just described), which were 20 mm in diameter.

---

[10] This Bulletin, 11, p. 177; 1914. "Galvanometer Mirrors."

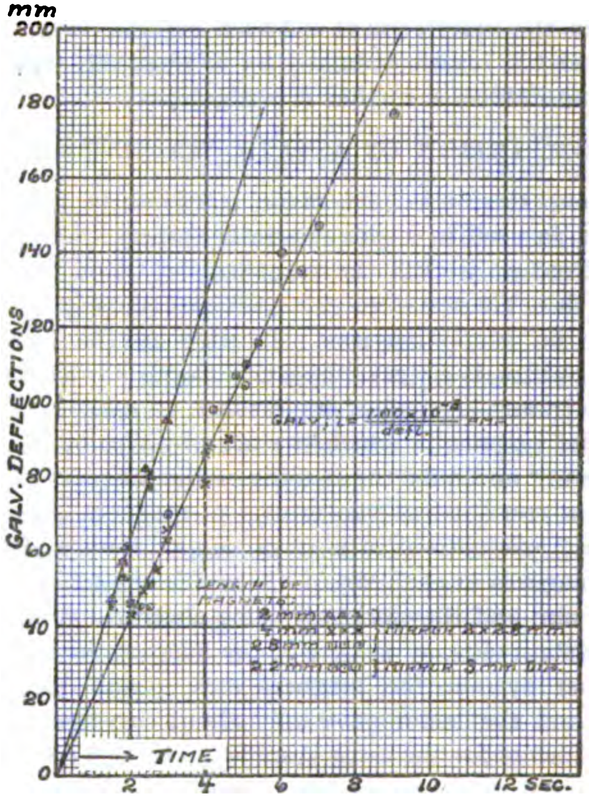


FIG. 3.—*Variation of sensitivity with length of needle*

IV. TEST OF SHIELDING AGAINST MAGNETIC DISTURBANCES

The greatest advances in the improvement of the Thomson galvanometer in recent years have resulted from providing it with a suitable protection against magnetic perturbations and air currents. The latter can, of course, be eliminated by placing the instrument in an evacuated inclosure (which procedure increases the sensitivity) but new difficulties are then encountered. In the present design, in which the coils are embedded in blocks of Swedish iron, there is but little air space, and the unsteadiness of the galvanometer needle by air currents is eliminated. In such an instrument a current sensitivity of $i = 2 \times 10^{-10}$ amperes (scale at 2 *m*) is easily maintained.

From a theoretical standpoint Wills[11] has shown that, given the innermost and outermost radii of the system of three concentric hollow spheres or cylinders, the maximum shielding will be obtained when the inner and outer radii of the successive shells, and the air spaces separating them are in the same geometrical progression. Using transformer iron one could easily make up cylinders according to these specifications.

In practice it has been found desirable to use as much metal as possible and to place the iron shields as close as possible to the coils. In the earliest designs[12] the writer, following the custom then in vogue, mounted the coils in a brass frame (having an excessive air space) surrounded with wrought-iron gas pipe 30 cm in length, 7, 10, 15, and 20 cm in diameter, and 4 to 6 mm in thickness. The smallest of these shields caused disturbances, due to permanent magnetization, and was discarded. The shielding was improved by adding a cylinder made of transformer iron (about 20 cm high and 9 cm in diameter; 8 turns; thickness 0.4 mm) and a large outside shield 32 cm in diameter. This proved effective for a while, but, the magnetic disturbances in the vicinity of the laboratory becoming greater, the brass mounting was discarded and the coils were embedded in Swedish iron.[13] The fluctuation of the zero reading on the galvanometer scale is shown in Fig. 4 (dotted curve represents a second series of observations), when the coils were in a brass mounting (galvanometer No. 1), the shields consisting of the "inner shield" of transformer iron (about 16 turns; thickness 0.4 mm) and four cylinders of iron pipe, 12, 15, 20, and 32 cm, respectively, in diameter. In Fig. 5 is shown the fluctuation of the zero scale reading of galvanometer No. 2, consisting of the Swedish-iron mounting, the so-called inner shield of transformer iron (9 cm in diameter, 6 mm in thickness; about 16 turns; thickness 0.4 mm), and a cylinder of single thickness of soft iron pipe 20 cm in diameter. (See Table 2.) The observations on these two galvanometers, which stood side by side, were made in close succession, i. e., observations were made for three minutes, alternately, upon each galvanometer. They illustrate the much greater steadiness of the suspended needle system when in the ironclad (Swedish-iron) mounting. The next step was to add further shields to the ironclad mounting and cover the top with a layer of transformer iron about 5 mm in thickness. The complete shielding outfit of this galvanometer consisted of the Swedish-iron mounting, the "inner shield" of transformer iron, and the iron cylinders 12, 15, 20, and 32 cm in diameter. As shown in Fig. 6, the fluctuations in the zero scale reading are reduced to 0.2 mm, the galvanometer sensitivity being $i = 5 \times 10^{-10}$ ampere and the complete period being less than three seconds. From this it may be seen that in view of the fact that only a few seconds of time are required to make a reading, one can easily obtain plenty of good observations without being obliged to make

---

[11] Wills, Phys. Rev., 24, p. 243; 1907.

[12] This Bulletin, 4, p. 392; 1908.

[13] This Bulletin, 9, p. 61, 1912; 11, p. 132, 1914.

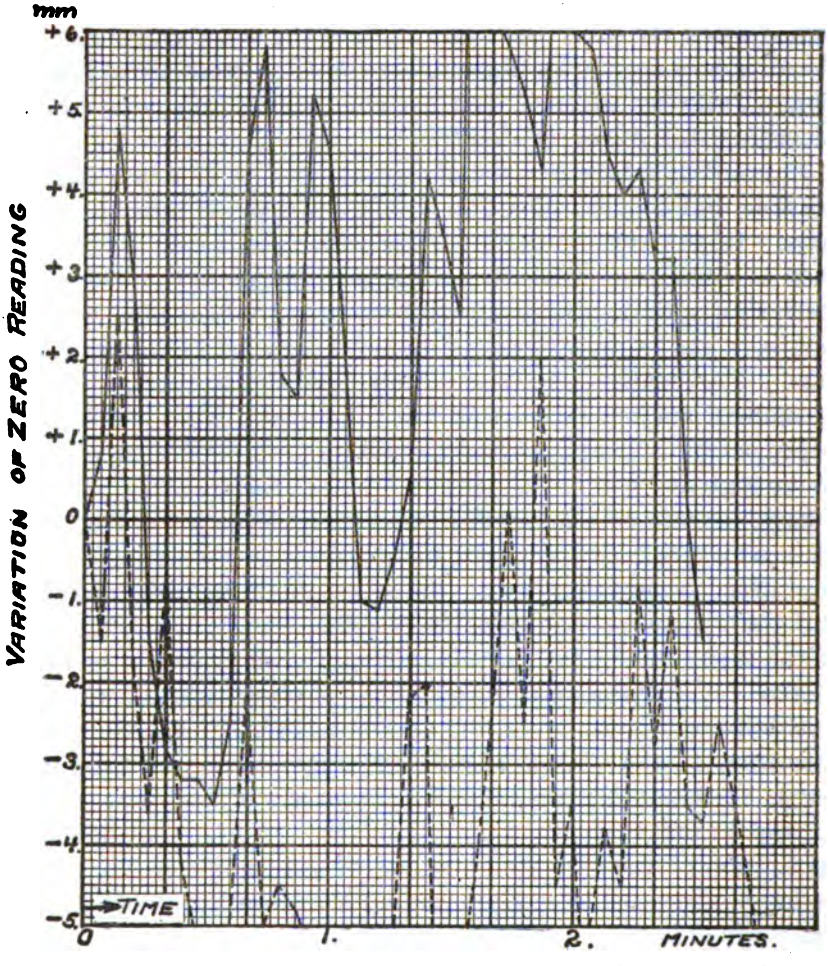


FIG. 4.—*Fluctuation of galvanometer needle when mounted in a brass frame and shielded with several cylinders of gas pipe*

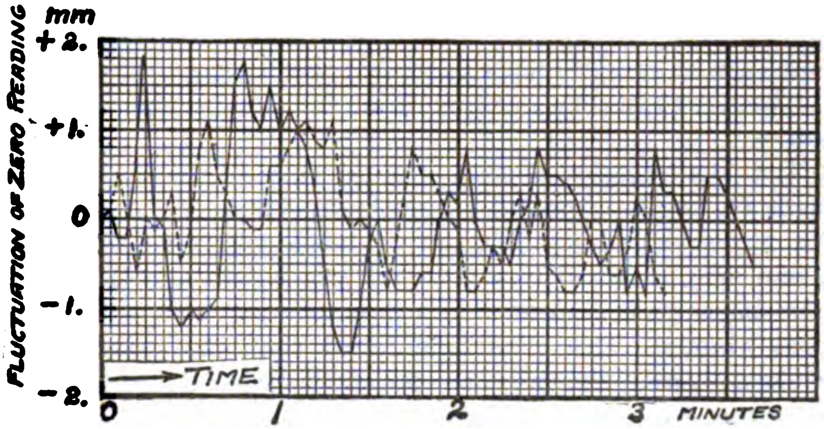


FIG. 5.—*Fluctuation of zero reading of the needle in an ironclad mounting, surrounded with one cylinder of gas pipe 20 cm in diameter*

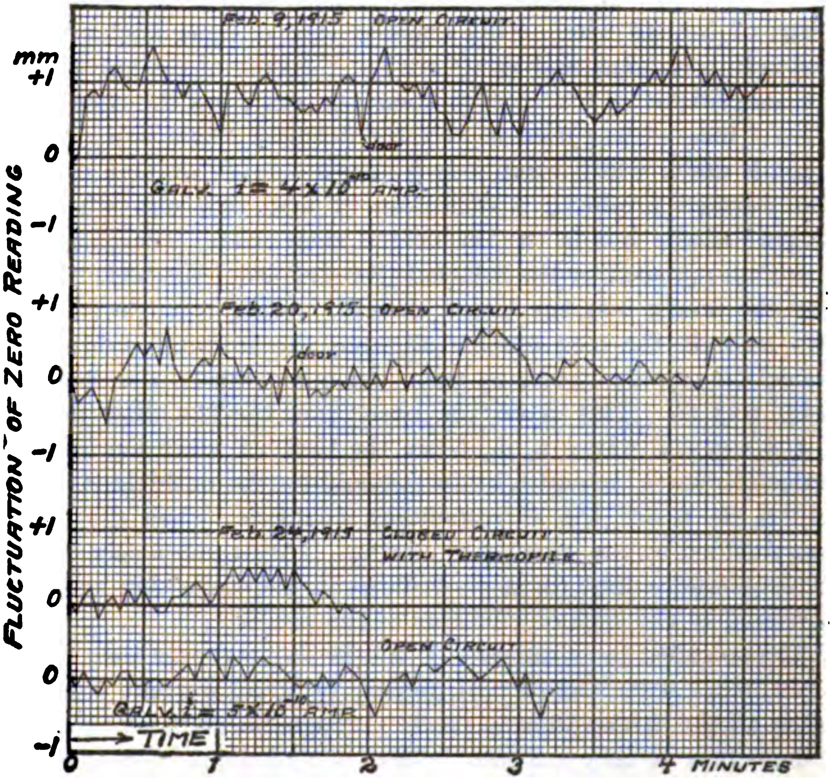


FIG. 6.—*Fluctuation of the zero reading of ironclad galvanometer No. 2 when all the shields were in place*

measurements when the zero is unsteady. From the behavior illustrated in Fig. 6 it is evident that ordinary magnetic disturbances can be greatly reduced and that the Thomson galvanometer can be given a much wider application than has been possible heretofore.

The determination of the numerical value of the shielding was made on another ironclad galvanometer which is a duplicate of No. 2, just described. The test was made with a single magnet, 2 mm long, attached to a glass rod which held also the mirror. This magnet was suspended in a glass tube provided with a plane glass window. This glass tube rested upon the concrete base which supported the galvanometer and shields. The latter were, of course, temporarily removed and the magnet was suspended at the same height from the support as obtained when it was suspended in the ironclad (Swedish-iron) mounting. The deflecting field was produced by an electric current passed through a solenoid about 31 cm long, 5.5 cm in diameter, and containing about 280 turns of No. 16 wire. This solenoid was at right angles to the magnetic meridian and was placed at the base of the galvanometer support, at a distance of about 42 cm from the needle. A control magnet was used to give the needle a single swing of two seconds under which conditions a current of 0.04 ampere through the solenoid produced a deflection of over 250 mm when the magnet needle was in the unshielded glass tube. The glass tube was then replaced by the ironclad (Swedish-iron) support, "I. C.," and the needle was suspended therein. Using a single swing of two seconds the 0.04 ampere through the solenoid produced a deflection of only about 25 mm. In other words, the shielding ratio was 10. This is on the basis that the shielding ratio is $d_1 t_2 i_2 \div d_2 t_1 i_1$ where t_1, d_1, i_1 are the time of vibration and the deflection for a current i_1 in the solenoid for the unshielded needle and t_2, d_2, i_2 are the corresponding quantities when the needle was shielded by the ironclad mounting. It was previously proven experimentally that for a given current, the deflection was proportional to the time of vibration of the needle.

The so-called inner shield ("I. S." in Table 2) was then put in place, when a current of 0.04 ampere (a larger current was used when all the shields were in place) through the solenoid produced a deflection of only 4.2 mm, which is equivalent to a shielding ratio of 58. This was verified the following day, giving the mean values assembled in Table 3. The additional shields to this galvanometer consisted of five cylinders of extra heavy wrought-iron gas pipe, 25.5 cm in height and increasing in diameter from 12 cm for S_1 to 22 cm for S_5, as shown in Table 2. From the data given in Table 3 it is to be observed that the addition of one cylinder of wrought iron, S_1, produced a shielding ratio of 226; and that it required the complete set of five shields in order to produce a shielding ratio of about 1700. Covering the top of these shields with three sheets of transformer iron increased the shielding ratio to about 1800.

TABLE 2

Dimensions of Swedish Iron Mounting, I. C., and of Various Shields of Gas Pipe

[Outside dimensions of ironclad mounting, I. C., 4.8 by 5.0 by 9 cm. Length of all shields, 25.5 cm, except the inner shield, I. S., which was 16.5 cm in height.]

Shield	Inner diameter	Thickness of wall
Extra heavy:	mm	mm
I. S.	78	7
S_1	121	9.5
S_2	146	8.5
S_3	165	11.5
S_4	193	11.5
S_5	220	13.0
Single thickness:		
S_1	128	6
S_2	156	7
S_3	180	7.5
S_4	205	7
S_5	228	8

TABLE 3

Reduction in the Magnetic Disturbance of the Magnet Needle (the "Shielding Ratio") by Inclosing it in Various Cylinders of Extra Heavy Wrought Iron. (See Table 2)

Kind of shield	Shielding ratio
Ironclad mounting, I. C.	10.1
I. C.+I. S. ("inner shield")	57.5
I. C.+I. S.+S_1	226.0
I. C.+I. S.+S_1+S_2	373.0
I. C.+I. S.+S_1+S_2+S_3	675.0
I. C.+I. S.+S_1+S_2+S_3+S_4+S_5	1690.0
Ibid, covered with 3 sheets of transformer iron	1790.0
I. C.+I. S.+S_1+S_2+S_3+S_4+S_5 (all of single thickness)	1040.0
Using an astatic system:	
I. C.	18.0
I. C.+I. S.	71.0

Using five cylinders of single thickness (see Table 2 for thickness of material) wrought-iron gas pipe, instead of the same number of extra heavy cylinders just described, the shielding ratio was only about one-half as large. This shows the importance of using the heaviest shields that can be obtained. The total weight of iron in this galvanometer when using the extra heavy iron shields was over 64 kgs.

The shielding ratio is apparently only one-half that attained by Nichols and Williams.[14] It is to be noted, however, that they reduced their observations on the basis that the deflection produced is proportional to the square of the time of vibration. In the present test with all the shields in place, the time of vibration (single swing) happened to be four seconds instead of two seconds which obtained when the magnet was in the unshielded glass tube. On the basis that the deflection is proportional to the square of the period (which is true only for a vacuum galvanometer) the shielding ratio would be four times the value recorded. From all the experimental data at hand, concerning the time of swing of a galvanometer needle in air, the reduction of observations on the basis of the square of the period is erroneous. In this test conditions were closely the same as those which obtain in practice, excepting that an astatic system is less easily perturbed than a single needle. From the experimental work of Nichols and Williams the shielding ratio would be greatly increased by annealing the iron cylinders. In the present test the cylinders were not annealed.

In view of the fact that this shielding test was not applied to galvanometer No. 2 (Fig. 6) it may be added that its zero reading is as steady as the new galvanometer, showing that its shielding is sufficient in the present location, although it can not be as effective as the new combination which employs the extra wrought-iron cylinders just described.

V. TEST OF A VACUUM GALVANOMETER

In a previous paper [15] experiments were described on the behavior of a certain galvanometer suspension in a vacuum of less than 0.1 mm. in which the sensitivity was not proportional to the square of the period, as was supposed to obtain when the air damping is removed. Evidently there was considerable damping by the residual air. It was therefore of interest to make a further test on a very light magnet system in a high vacuum produced by removing the residual air by means of hot metallic calcium. Furthermore, it was of interest to make the test on a single set of magnet needles instead of an astatic system, in view of the excellent magnetic shielding just described, which makes it possible to dispense with the astatic system of magnet needles. In the test just described on magnetic shielding, it was noticed that the single set of magnet needles was practically as well shielded as the astatic system consisting of two sets of magnet needles. The obvious advantages in using a single set of magnet needles are (1) the requirement of but two galvanometer coils and (2) the reduction of the weight of the magnet system; thus practically doubling the sensitivity. Theoretically, of course, each set of magnets in an astatic system is affected by the current in the adjacent coils. thus increasing the deflection. Hence, one set of magnet needles would not be so efficient magnetically in spite of the increase in sensitivity due to decrease in weight. In other words, the sensitivity would not be quite doubled by simply removing one set of magnets from the astatic system. Owing to mechanical difficulties in construction it is frequently found difficult to obtain agreement between theory and practice. However, in the present case there is a close agreement with theory. It will be shown presently that the single set of magnets, in an astatic pair, is not quite twice as efficient (sensitive) as the astatic pair.

---

[14] Nichols and Williams, Phys. Rev., 27, p. 250; 1908.

[15] This Bulletin, 11, p. 177; 1914.

In the experiments now to be described the sensitivity of an astatic system in air was determined for different periods. The lower set of magnets was then removed (see Fig. 2 for photographs of astatic magnet systems) and the sensitivity was again tested for different periods. In both tests only the two upper (21-ohm) coils of the galvanometer previously employed in measuring heat from stars (Fig. 2) were used. The coils were joined in parallel giving a resistance of about 10 ohms. A still higher sensitivity than was attained in the present tests is to be expected by using two coils of low resistance joined in series.

For making the test in a vacuum the galvanometer was placed on a ground glass and covered with a glass bell jar about 9 cm in diameter, which prevented the use of the "inner shield" of transformer iron. However, the other shields of soft wrought-iron gas pipe were sufficient to quite effectively shield the single set of magnets.

The vacuum was maintained by means of metallic calcium[16] in a quartz-glass test tube, heated with an alcohol lamp. This was of course, merely a temporary arrangement for making this test. The vacuum galvanometer for star work will, of course, be properly designed as the results of these various tests.

---

[16] This Bulletin, 11, p. 185; 1914.

The astatic system of magnets used in these tests consisted of two groups of magnets. Each group consisted of four magnets from 1.4 to 1.6 mm in lenght, 0.25 mm in width, and 0.1 mm in thickness. The glass staff was 0.1 mm in thickness. The two groups of magnets were 29 mm apart; and the glass mirror was attached at the center of the staff. This glass mirror was platinized by cathode disintegration. It was made from especially prepared glass [17] 0.15 mm in thickness. Its surface was 1.3 mm by 1.6 mm. By using a telescope with a very good eyepiece, a still smaller mirror could be used. In photographic registration a much smaller mirror could be used, thus increasing the sensitivity.

The current used to excite the galvanometer was $i = 1.45 \times 10^{-8}$ amperes. This produced the deflections shown in curve 1, Fig. 7, the scale being at 1.4 m. Using this suspension the deflection is directly proportional to the period, as reported in previous papers, when using heavy suspensions in air.

On removing the lower set of magnets, the weight of the suspension (which was now about 1.8 mg) was so much reduced that slight tremors were noticeable. As shown in curve 2, Fig. 7, the sensitivity was about doubled by removing the lower set of magnets. This curve gives observations made on two different days, the values being slightly lower on the second day. The air damping is very marked as shown by the curvature in the graph.

On reducing the air pressure to about 0.1 mm the sensitivity of this set of magnets, for a two-second swing is 2.5 times that of the astatic system. Finally, by removing the residual air by heating the metallic calcium, the sensitivity is proportional to the square of the period (curve 3, Fig. 7), so that by changing the time of single swing from two seconds to six seconds the sensitivity is increased from $i = 9 \times 10^{-11}$ amperes to $i = 1 \times 10^{-11}$ amperes. The previous work on stars indicated that a single swing of five to six seconds is easily controlled.

With all the air removed a new difficulty arises from the lack of damping of the galvanometer needle, which keeps swinging back and forth 10 to 15 times before coming to rest. In practice it may therefore be better to have a small amount of air present for damping, instead of providing other means for bringing the needle to rest.

---

[17] This Bulletin, 11, p. 177; 1914.

The performance of the galvanometer suspension used in 1914 in measuring the radiation from stars [18] is shown in curve 5, Fig. 7, the time of single swing being about three seconds and the sensitivity being about $i = 2 \times 10^{-10}$ amperes for a scale at 2 m. The sensitivity of that suspension in air is therefore somewhat (20 per cent) higher than the one used in the present test. Hence, using

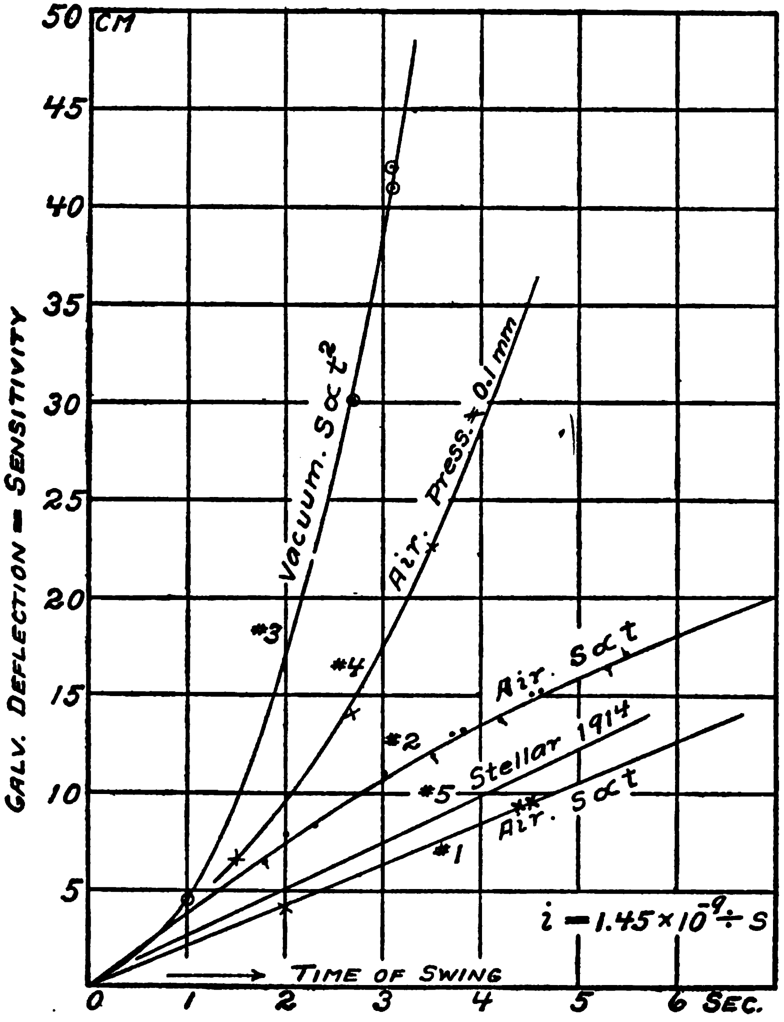


FIG. 7.—*Test of current sensitivity of a galvanometer in air and in a vacuum*

only one set of magnets of this astatic pair, a still higher sensitivity is to be expected than was attained with the suspended system just described.

---

[18] This Bulletin, 11, p. 613; 1915.

From the foregoing tests it is evident that the sensitivity of this outfit is about 10 times (for the same swing) that used in the preceding measurements of heat from stars. This was accomplished by using a lighter suspension in a vacuum. It is to be remembered, however, that a lighter suspension had been provided for the previous work, but not having a separate pier for the galvanometer no attempt was made to use a higher sensitivity than $i = 1 \times 10^{-10}$ amperes.

These tests are, of course, only preliminary and of a cursory nature. By concentrating one's efforts upon the vacuum galvanometer as it will be used (by trying various suspensions) it appears possible to produce a sensitivity of $i = 5 \times 10^{-12}$ amperes on a single swing of five to six seconds, so that by reading to a fractional part of a scale division one can observe deflections caused by currents of the order of 1×10^{-12} amperes. Such a high sensitivity is possible with the set of magnets used in the present test by lengthening the time of swing from eight to nine seconds. The general experience in radiometric work is that, at certain times, meteorological conditions are sufficiently steady so that the time of single swing of the galvanometer can be increased to 12 or 15 seconds (observations on curve 2, Fig. 7, were made on a single swing of 16 to 17 seconds), thereby enabling one to obtain a sensitivity of $i = 1 \times 10^{-12}$ amperes, and, by reading fractional parts of a scale division, 5×10^{-13} amperes.

For controlling such a high sensitivity it will be necessary to design the instrument so as to shield it from static changes such as were observed in the previous measurements of stellar radiation,

In the previous paper,[19] giving the measurements on the radiation from stars, the conclusion arrived at was that it is desirable to increase the sensitivity of the stellar radiometer 20 times; by increasing the sensitivity of the thermopile 2 times and the galvanometer 10 times. The foregoing experiments indicate the manner in which the galvanometer sensitivity may be easily increased by 10 to 15 times that used in the previous investigation.

---

[19] This Bulletin, 11, p. 613; 1915.

VI. SUMMARY

The present paper gives the results of an investigation of the force exerted by various galvanometer coils as compared with a set of three coils used as standards. Some of the coils were wound according to theoretical requirements, while others were wound empirically. Numerical data are given relating to the force exerted by coils having various resistances. A simple coil is described, wound with a single size of wire (No. 28) which was found to be very efficient.

A 9-ohm coil (see test on the 8.6-ohm coil) is described which is very efficient and is well adapted to be used with the bismuth-silver thermopiles previously described.

A comparison is made of various astatic magnet systems and data are given showing the importance of using small mirrors in order to increase the sensitivity.

Experiments are described on shielding the galvanometer needle from external magnetic disturbances. The galvanometer coils are mounted in cavities cut into blocks of Swedish iron, which reduce the air space and act as a magnetic shield. This elimination of convection currents greatly improves the steadiness of the needle system. Various shields are described, consisting of laminated cylinders made from transformer iron and solid cylindrical shells cut from wrought-iron gas pipe. By imbedding the galvanometer coils in blocks of Swedish iron which are surrounded by cylindrical shells of transformer iron and of wrought iron, the effect of external magnetic perturbations upon the astatic needle system is easily reduced to 1/2000 of its original value.

Experiments on a vacuum galvanometer are described, in which a sensitivity was attained which is more than tenfold that used in the writer's previous work on stellar radiation.

WASHINGTON, October 8, 1915.

APPENDIX

NOTE I. MOUNTING FOR VACUUM THERMOPILES

The object of this note is to summarize some of the results given in previous papers on thermopiles and to describe a new mounting for vacuum thermopiles.

During the past few years there has arisen a need for a sensitive radiometer for measuring light stimuli which are used in various physical, physiological, and psychological problems. The instrument must be simple in operation so that it can be used by experimenters who have had but little experience in radiometry. The linear thermopile of bismuth [20] with connecting wires of copper or silver was designed with the view of supplying this need of a sensitive radiometer which can be operated in air, thus avoiding an additional equipment for maintaining a vacuum. However, as mentioned in previous papers, the linear thermopile is not an efficient instrument in comparison with a single thermojunction. For example, a linear thermopile of 16 junctions is only four times as sensitive as a single junction of this same instrument. In a vacuum, such as one can easily produce with an oil pump, the sensitivity of the linear thermopile is doubled, so that, by reducing the gas pressure to 0.005 to 0.01 mm, the sensitivity of the linear thermopile is from eight to ten times that of a single junction of bismuth-silver (or copper) in air.

Copper or silver connecting wires are used in the linear thermopile in order to maintain a low resistance. When using a single thermocouple the resistance is of minor importance. It is therefore possible to increase the radiation sensitivity of the thermojunction by using a metal which has a lower heat conductivity than copper or silver. In the thermocouples used in measuring heat from stars [21] the radiation sensitivity was doubled by connecting the bismuth with platinum instead of silver wire. The radiation sensitivity of the bismuth-platinum thermocouple was further increased four to five times when it was used in a vacuum maintained by means of metallic calcium, so that the total radiation sensitivity was about ten times that of a single bismuth-silver thermojunction used in air. In other words, this single junction of bismuth-platinum, in a high vacuum, was about twice as sensitive as a linear thermopile in air, having 16 junctions of bismuth-copper (or silver) and having sixteen times the receiving surface. However, greater care is required in operating the vacuum thermocouple.

---

[20] This Bulletin, 9, p. 7, 1912; 11, p. 132, 1914.

[21] This Bulletin, 11, p. 163, 1914; 11, p. 613, 1915.

The method of construction of a radiometer depends entirely upon the manner in which the instrument is to be applied. The most common use of a thermopile is no doubt in connection with spectral energy measurements, and the present discussion has reference to this particular application. As mentioned in previous papers, but little work has been done on the radiation from solids and gases in the visible and ultra-violet part of the spectrum. This is attributable chiefly (1) to the low intrinsic brilliancy of most of the present-day illuminants, (2) to the low light-gathering power of the telescopes used in the spectrometers, and (3) to the low sensitivity of the radiometers. The amount of energy to be measured is defined by the width and height of the spectrum. By using a curved radiometer slit which fits the curvature of the image of the spectroscope slit it is possible to utilize a greater height of the spectrum than is possible with the slits which are usually supplied by makers of spectroscopic apparatus, and the amount of radiant energy available is proportionately increased. In cases where the absorption of the mirror is negligible or where corrections can be applied to the energy measurements it is more efficient to use a single thermojunction and concentrate the whole spectral line upon it by means of a concave cylindrical mirror than to use a linear thermopile which intercepts the whole length of the spectrometer slit.[22] By this means one will obtain about sixteen times the sensitivity of a single thermojunction, whereas a sensitivity (a galvanomer deflection) of only four times that of a single junction would be produced by a linear thermopile of 16 junctions which intercepted all the radiations falling upon the spectrometer slit.

The thermopile, while more steady than a bolometer, is not entirely free from disturbances by air currents. It is therefore desirable to use it in a well-constructed chamber which can be evacuated. This increases both the steadiness of the galvanometer readings and the sensitivity of the radiometer. It is desirable to be able to use the instrument in an independent mounting as well as when attached to a spectroscope. Both the vacuum arrangement and the interchangeable mounting are therefore embodied in a new design shown in Fig. 8, which shows the container for the thermopile raised, thus exposing the spectrometer slit, *S*. The vacuum container is provided with a wide (12 mm) flange and the cover is sufficiently thick (5 mm) to prevent warping, so that the vacuum is more easily maintained than in the design previously described. The opening for admitting radiation upon the thermopile is covered with a window, as shown in Fig. 4 of the previous paper.[23] The lead wires of the thermopile are brought out of the container by passing them through a fiber bushing and attached to copper binding posts, as shown in the photograph. A bit of Chatterton compound is applied at the point where the wires emerge from the fiber bushing. In this manner it is possible to easily produce an air-tight connection to the thermopile.

---

[22] This Bulletin, 11, p. 169; 1914.

In the designs previously described, the heavy copper binding posts, which acted as heat reservoirs, extended into the containing vessel, and the lead wires to the thermopile were attached on the inside of the receptacle. In this manner air currents could not easily cause temperature fluctuations in the wires. In the present design the conducting wires to the thermopile are attached, within the receptacle, to heavy (No. 24) copper wires which pass through the insulating bushing to the heavy copper binding posts, as shown in Fig. 8. Air currents across the exposed parts of these wires may cause temperature fluctuations which may be communicated to the thermopile. The exposed parts of these heavy lead wires between the binding posts and the container are therefore covered with rubber tubing in order to shield them from air currents. The lead wires to the galvanometer are heavy "twisted lamp cord," as previously described.

---

[23] This Bulletin, 11, p. 156; 1914.

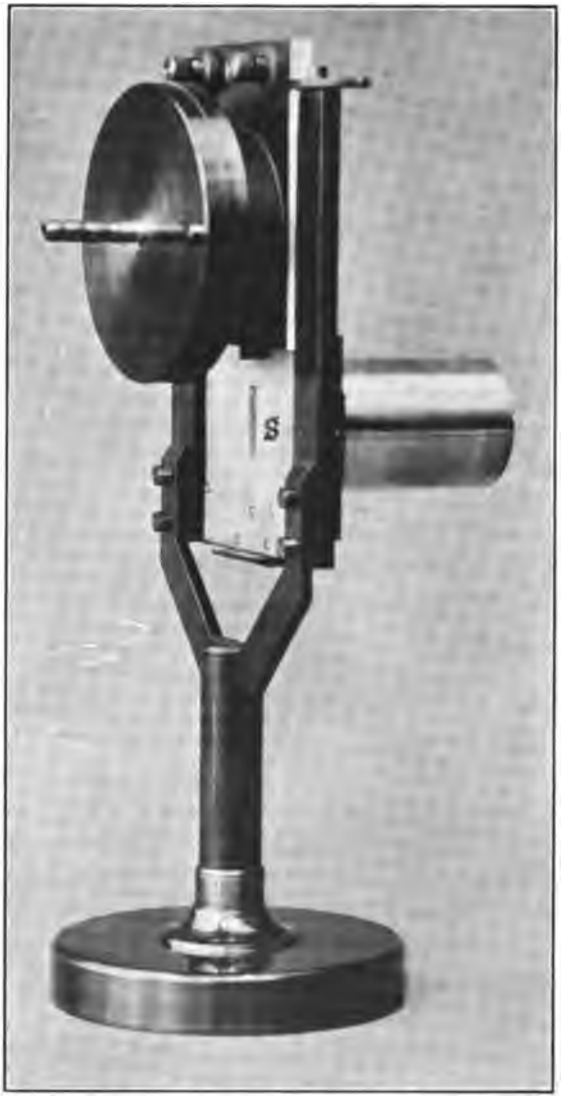


FIG. 8.—*Mounting for a vacuum thermopile which can be attached to a spectrometer*

VOLUME EFFECT IN THE SILVER VOLTAMETER

By E. B. Rosa and G. W. Vinal

In several of our earlier papers[1] we have described a phenomenon which we have called the "volume effect." This consisted in an excess weight of deposit in the large-size voltameters over that in the smaller sizes which were used simultaneously in series. This difference was seldom very large and was generally attributed to experimental error prior to the middle of February, 1910. By this time, however, so many cases of the excess deposit in the larger sizes of voltameter (both porous cup and siphon forms) had occurred that a careful analysis of the preceding results was made. The ratio of the deposit in the large-size voltameter to the deposit in the small size was computed for every reliable experiment where large and small voltameters were used in series and were identical in all particulars except the size of the cups and the volume of the electrolyte. Shortly after this we prepared a statement of our results for the International Technical Committee, and briefly discussed[2] this volume effect. Although we have referred to it more in detail in our later publications[3] and have given quantitative evidence of its reality and have prepared a theory to account for it, misunderstanding has arisen concerning it and some writers have even questioned its reality. Von Steinwehr[4] has stated that since we have observed it only in the porous-cup form of voltameter (which, however, is not the case) it must be due to an error caused by the porous cup, and hence the porous cup should be discarded. Richards and Anderegg,[5] finding their own voltameters (in two experiments) to show an excess deposit in the large size before heating the cups and deposits to redness, concluded that the excess weight was due to mother liquor imprisoned between the surface of the cup and the crystals, the amount being greater in the large cup because of the greater surface. More recently, Jaeger and von Steinwehr[6] have stated that there are no systematic experiments showing the volume effect in any other form of voltmeter but the porous-cup form. We have previously called attention to the fact[7] that the volume effect was evident in Lord Rayleigh's experiments using the filter-paper voltameter. Averaging all of his comparisons of large and small voltameters there is an outstanding difference of 14.5 in 100 000, the large voltameters usually having the heavier deposit. In only 1 case out of 10 did his small voltameter show an excess of deposit over the large size. Jaeger and von Steinwehr[8] express the opinion that the accuracy of Lord Rayleigh's results is not sufficient to establish the reality of this difference. This might be granted if there was no other evidence, but at least it tends to confirm the large amount of evidence we shall present below as to the reality of the volume effect.

---

[1] This Bulletin, 9, pp. 154, 168, 514.

[2] Supplement to Report of the International Committee, p. 9; 1912.

[3] This Bulletin, 10, p. 530; 13, p. 167.

[4] Zs. f. Instrk., 33, p. 321; 1913.

[5] J. Am. Chem. Soc., 37, p. 20; 1915.

In dealing with such a phenomenon as the volume effect where the differences are not far removed from the experimental error, we can best treat a large number of observations by statistical methods. Since the volume effect involves a comparison of two voltameter deposits, each of which is subject to an experimental error, it is natural that the experimental error of the ratio should be larger than for the single determinations.

If S_1 represents the weight of deposit in a large voltameter and S_2 the weight of deposit in a small voltameter then we may put

$$Z=\frac{S_1}{S_2}$$

If the probable error of S_1 is r_1 and of S_2 is r_2, then the probable error of Z is R as defined by the equation:

$$R^2=\left(\frac{\delta Z}{\delta S_1}\right)^2 r_1^2+\left(\frac{\delta Z}{\delta S_2}\right)^2 r_2^2 \tag{1}$$

Equation (1) after differentiating becomes

$$R^2=\left(\frac{1}{S_2}\right)^2 r_1^2+\left(\frac{S_1}{S_2^2}\right)^2 r_2^2 \tag{2}$$

dividing (2) by Z^2 we have

$$\left(\frac{R}{Z}\right)^2=\left(\frac{r_1}{S_1}\right)^2+\left(\frac{r_2}{S_2}\right)^2 \tag{3}$$

---

[6] Zs. f. Instrk., 35, p. 225; 1915.

[7] This Bulletin, 10, p. 530.

[8] Loc. cit.

Each term of (3) represents a percentage probable error. The magnitudes of $\frac{r_1}{S_1}$ and $\frac{r_2}{S_2}$ are found by referring to our previous papers. For example, if we use the second series of quantitative results,[9] we find by a computation 0.0034 per cent for the large size and 0.0026 per cent for the small size. These are slightly higher than for our last and best work. Substituting these values in (3) we obtain as the value of R, since Z is practically unity

$$R = 0.0043 \text{ per cent.}$$

This, then, is the probable error of a single determination of the volume effect for the cases in which the salt was used as purchased.

To make the best use of all the data at hand we have subdivided our results into three classes. The first class includes all of our determinations made with the ordinary market variety of c. p. silver nitrate and it includes salt purchased from J. T. Baker & Co., of America; Baird & Tatlock, of England; the Gold- und Silber-Scheide-Anstalt, of Germany; and Poulenc Frères, of France. The second class includes all of our determinations given in our latest and best work of the Part IV[10] (except where a direct comparison of size of voltameter was not available). In all the observations for class 2 the salt used for preparing the electrolyte was tested by our permanganate and acidity tests[11] and found satisfactory. Such samples of salt for class 1 as were tested by these same tests were not found satisfactory. The third class of results includes cases in which the electrolyte was purposely contaminated with filter paper or the extract of filter paper. Seven out of the nine of these determinations were made recently.

The analysis of our observations is perhaps most conveniently and convincingly presented by means of two diagrams. In the first (Fig. 1) we have only the results using the porous-cup voltameter, in order that the results so obtained may be compared with those of the second diagram (Fig. 2), which includes the results using the Kohlrausch voltameter (points marked K), the siphon, the new form of Mr. Smith, and the filter paper form (F). For each diagram the abscissae are ratios of the volume of electrolyte in the large voltameter to that in the small size and the ordinates are ratios of the silver deposit in the large voltameter to that in the small size. Electrolytes used as the salt was purchased without further purification and without satisfying the permanganate and acidity tests are designated by solid black dots. The second class—that is, electrolytes made from purified salt which was satisfactory by our tests—is designated by the circles, and the third class, of especially contaminated electrolytes, is represented by

---

[9] This Bulletin, 9, pp. 504, 506.

[10] This Bulletin, 10, p. 475.

[11] This Bulletin, 9, p. 524.

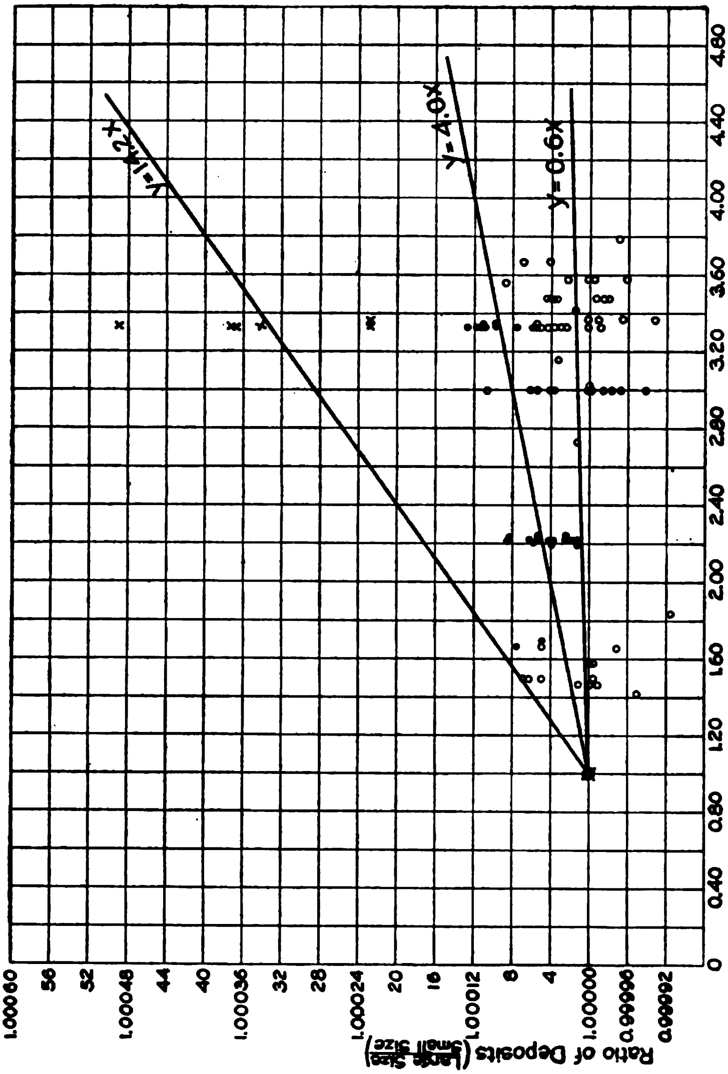


Fig. 1.—*Observations with the porous-cup voltameter*

crosses. Each point, therefore, represents the ratio of the deposit in the large size to that in the small size, the two voltameters being exactly similar in all respects but the volume of electrolyte. The only exception to this is in the case of the siphon voltameter. It is not practicable to use a siphon voltameter having as small a volume as our ordinary small voltameters (90 to 100 cc) since the resistance of such an instrument would be too high. In this case, therefore, we have had to compute the ratio of the deposit in the

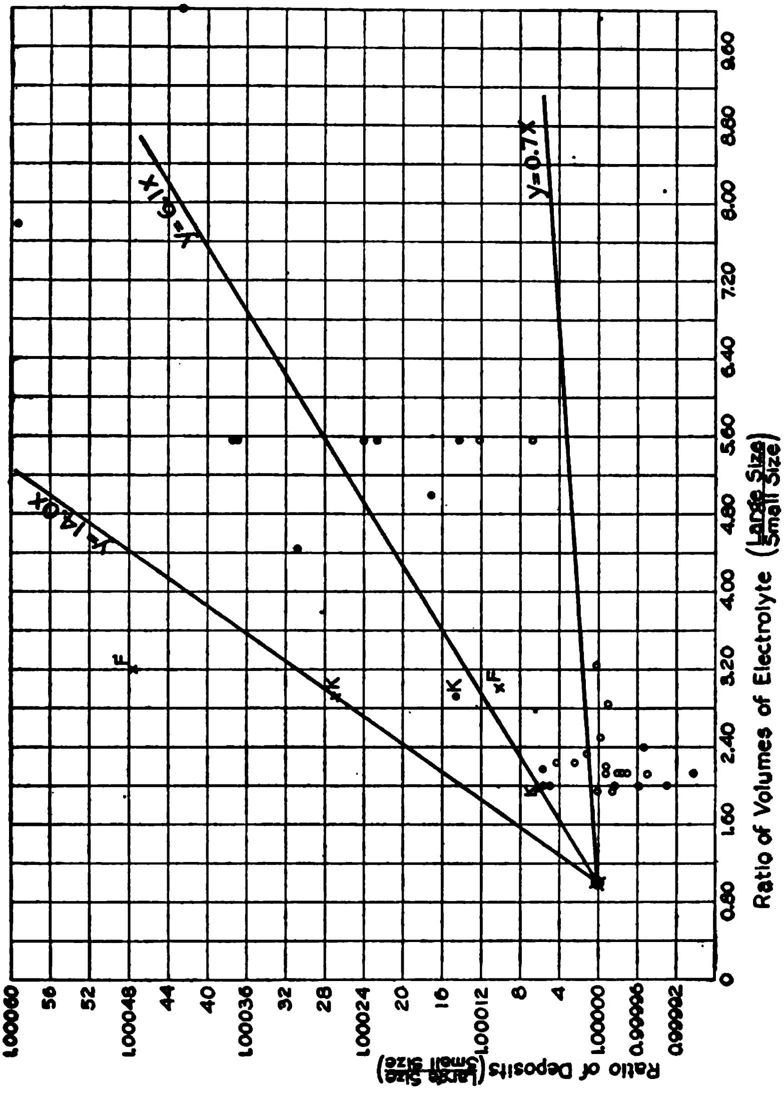


FIG. 2.—*Observations with the Kohlrausch (points marked K), the filter paper (points marked F), the Smith (points unmarked for ratios less than 4.00), and the siphon (points unmarked for ratios greater than 4.00) forms of voltameters*

siphon voltameter to the deposit in a small porous-cup voltameter used simultaneously. However, if all the siphon determinations were thrown out on this account the essential facts would remain the same.

We may now set down certain observations regarding these two diagrams which we think are justified by the results.

1. In no case did the ratio of deposits *from electrolytes as purchased* fall below unity. This means that the deposit in the large-size voltameter *was always* greater than in the small size. This is equally true *for all the forms of voltameter used.* There were 26 such observations with the porous-cup voltameter, 9 observations with the siphon form, 2 observations with the Kohlrausch form, and 1 with the new form. Total number of observations, 38.

2. In the case of *pure electrolytes*—that is, those represented by circles—the observations show that the deposits in the small voltameters often exceeded those in the large voltameters. In the case of the porous-cup voltameters there are 31 observations with a ratio of unity or greater and 25 observations with a ratio of less than unity. With the new form, 6 observations are greater than unity and 14 less. Two observations with the siphon form are greater than unity, and there are no observations at all with the Kohlrausch form. In all there are 39 observations greater than unity and 39 observations less than unity, showing no tendency whatever for the deposit to be heavier in the larger voltameter when the electrolyte is of the highest purity.

3. The observations with electrolytes purposely contaminated all lie far above the value unity. Six observations were made with the porous-cup voltameter, 2 with the filter-paper form, and 1 with the Kohlrausch form.

4. The above conclusions show that the general facts are the same for all of the different forms of voltameters with the several classes of electrolyte. This is clearly seen by referring to the curves. As the points are necessarily scattered we must depend on the statistical method of treating the observations. Thus, if we compute the equation of the *most probable* straight line representing porous-cup observations with pure electrolyte we obtain $y=0.6x$. If we do the same for the new form and siphon observations, we obtain $y=0.7x$, which is almost perfect agreement and closer than would be expected. The line in each case is nearly horizontal. The slight inclination appears to show that not all the electrolyte was perfectly pure, which of course was hardly to be expected. For the electrolyte as purchased—that is, slightly impure—we compute for the porous-cup voltameter $y=4.0x$ and similarly for the Kohlrausch, new form, and siphon forms $y=6.1x$. These are both very different from the line representing pure electrolytes, the porous-cup form showing, however, a smaller effect.

Taking the third class of electrolytes—that is, those which have been intentionally contaminated by the addition of filter paper—we compute for the porous-cup observations $y=14.2x$ and for the Kohlrausch and filter paper forms $y=14.0x$. This close agreement is of course accidental, but that the line has a much greater slope than for the second class is not accidental.

For convenience these equations have been computed on the assumption that the origin of coordinates is at the point $y=1$, $x=1$, and they are so given here to avoid the unnecessary complication of a term giving the intercept on the y axis. The value of these equations is merely to show the similarity of the values for the slopes, but if it is desired to write the equations referred to the true origin they can of course be very simply transformed.

If it be objected that because the siphon-voltameter deposits have been computed as the ratio to the deposit in the small porous-cup voltameter, as explained on page 451, an inspection of figure 2 will show that even omitting all these observations with the siphon no material change would be made in the slope of any of the curves, particularly in the case of the curve $y=6.1x$, which includes most of the siphon observations.

5. From the above it appears that our previous statements as to the volume effect were justified. The volume effect is caused by impurities in the electrolyte. It is not confined to the porous-cup voltameter, but occurs with all types, and is greater when the impurities in the electrolyte are greater and disappears when the electrolyte is strictly pure.

6. In a previous paper Vinal and Bovard [12] showed that the volume effect was not due to greater inclusions in the large-size voltameter, as supposed by Richards and Anderegg.[13]

We give in the table below some results recently obtained at the Bureau.

TABLE 1

Form	Contaminated			Uncontaminated		
	Large	Small	Δ	Large	Small	Δ
	mg	mg	mg	mg	mg	mg
Filter paper	4212.00	4210.00	2.00	4206.02	4205.07	0.95
Do	4069.59	4069.18	.41	4067.75	4068.19	−.44
Porous cup	4492.27	4491.06	1.21	4489.83	4489.49	.34
Kohlrausch	4244.26	4243.12	1.14	4241.99	4241.37	.62
Porous cup	4277.83	4276.86	.97	4275.99	4275.52	.47
	....	[a] 4276.72	1.11	....	....	....

---

[12] This Bulletin, 18, p. 147.

[13] Loc. cit.

[a] Very small size, only 40 cc.

The electrolyte used was an ordinary sample of c. p. silver nitrate, without further purification. This is marked "uncontaminated." It is seen from the above that this salt produced a volume effect of about 0.40 mg on the average, although the results with the filter-paper form are erratic, as might be expected. A portion of the same salt contaminated with filter paper was electrolyzed in two similar voltameters, and the results are given in the column headed "contaminated." It is seen that the effect is increased three times, on the average. In the last experiment we used the smallest porous-cup voltameter that we could arrange for a 4 g deposit. The electrolyte was only 40 cc. The table shows that it gave a smaller deposit than in what we have ordinarily called the small size (90–100 cc). The large-size voltameters contained about 300 cc. These volumes, in the case of the porous-cup voltameters, mean the volume of electrolyte outside the porous cup. We showed in a previous place [14] how effective a barrier the porous cup is between the anode and cathode.

It will be noticed in the table that the deposits from the contaminated solutions, although differing between themselves according to size, are all considerably inexcess of even the large-size voltameter containing the uncontaminated electrolyte. The reason for this will appear after a brief account of what we regard as the mechanism of this volume effect.

If we add some of the filter-paper extract [15] to a solution of silver nitrate in water, or put the filter paper directly in the electrolyte, marked changes in the condition of the solution take place. The filter-paper extract is a basic organic colloid [16] which produces a reducing action [17] on the silver nitrate. As the reduction proceeds important changes in the acidity [18] of the solution take place and the reduced silver appears in colloidal form.[19] It may become visible as a colloidal solution in cases where the filter paper contamination is considerable. The colloidal particles travel slowly to the cathode [20] under the influence of the electric current, and they are also helped along in this direction by the convection currents of liquid. The denser liquid from the region of the anode falls to the bottom of the cup and displaces upward the impoverished liquid at the cathode surface.[21] Probably each particle of colloidal silver drags along with it some of the organic colloid, which acts as a protective colloid[22] and prevents the rapid precipitation of the silver by the unreduced electrolyte.

---

[14] This Bulletin, 9, pp. 201, 220, 510.

[15] This Bulletin, 9, p. 237.

[16] This Bulletin, 9, p. 239.

[17] This Bulletin, 9, p. 237.

[18] This Bulletin, 9, p. 247.

[19] This Bulletin, 9, p. 238.

[20] This Bulletin, 9, p. 219.

[21] This Bulletin, 9, p. 269. (See Fig. 27 of Part II.)

In the contaminated electrolyte we have, therefore, a very large number of silver particles each of which is an aggregate of a large number of silver atoms. These are gradually swept along toward the cathode, and as each particle reaches the cathode it deposits its load of silver and organic matter[23] and also delivers up its charge, but the amount of electricity so transported is not commensurate with the mass of material laid down on the cathode. In this way an excess weight of deposit over that calculated for a univalent ion is produced, and this may be further increased by a somewhat greater inclusion[24] of the mother liquor, which is made possible by the colloid breaking up the crystalline structure of the deposits.

The rate at which this colloidal matter is swept out of the solution will depend upon the density of the electric current. At the beginning of an experiment we may justly assume that the number of colloidal particles per cubic centimeter of the electrolytes in contact with the cathode is the same in both large and small voltameters. When the electric current starts, the greater intensity of the current in the small voltameter due to the smaller cathode area will sweep the colloidal particles out of the solution at a greater rate than in the large size. Consequently, the electrolyte contiguous to the cathode in the small voltameter will become impoverished as to colloidal matter; that is, it is purified. The number of colloidal particles which will subsequently deposit per second diminishes for lack of the colloidal matter. However, the effect of the electric current and the convection currents of liquid, which arise because of the changing densities of the solution at the anode and cathode will replenish, impart, the colloidal matter to the depleted cathode solution. In the large voltameter the forces drawing the colloidal matter out of the solution at the cathode are less severe, as we have mentioned above, and in addition the convection currents of liquid are less impeded by the anode and its porous cup or glass trap, so that the solution on the face of the cathode is freed from colloidal matter more slowly than in the small voltameter. There is, of course, a greater supply of the colloidal particles in the voltameter having the greater volume of electrolyte. It is reasonable, therefore, to anticipate that more colloidal particles will be deposited in a large voltameter than in a small one during the two hours that the current flows. Consequently, the deposit in the large cup will be heavier than the deposit in the small cup. (See Fig. 3.)

---

[22] This Bulletin, 9, p. 239.

[23] This Bulletin, 9, p. 241.

[24] This Bulletin, 13, p. 167.

Probably there are some colloidal particles even in our purest solutions. We have never found a solution, on examination by the ultramicroscope, entirely devoid of colloidal particles; but in a strongly contaminated solution the colloidal particles are increased in number thousands of times. It is not surprising, therefore, that even in the small voltameter we should find an excess of deposit over that in voltameters which contain pure or nearly pure solution. The last experiment given in the table shows that the very small voltameter gave a smaller deposit than our ordinary small size with impure electrolyte; but even this is in excess of the large voltameter containing purer electrolyte, which, however, was not quite pure.

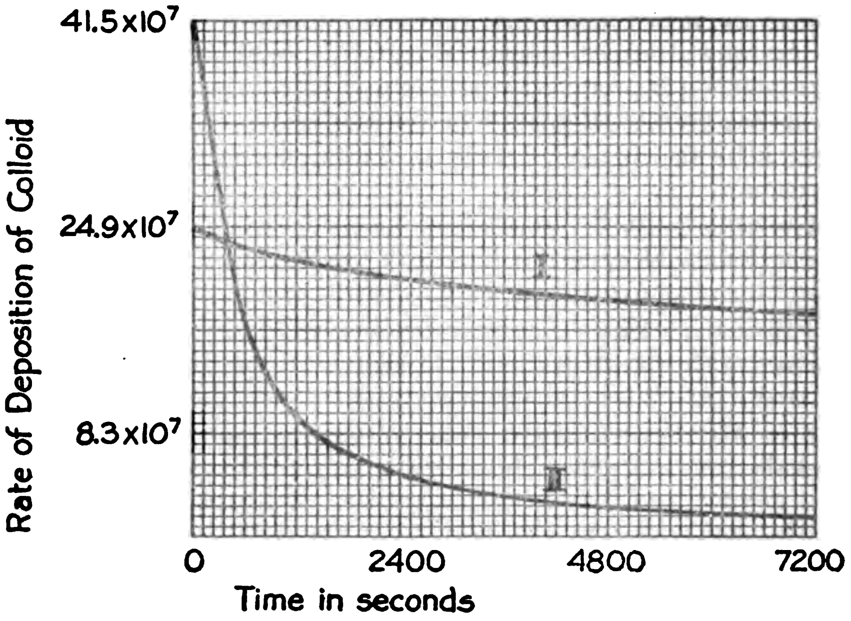


FIG. 3.—*Hypothetical curves illustrating the theory of the volume effect*

These curves are based on an average case in which the excess of deposit in the large voltameter over that in the small voltameter is 0.65 mg. It is assumed that the average diameter of the colloidal particles is 0.05μ from which we compute that 1 × 10^{12} more particles are deposited on the large cathode than on the small cathode. The area under each curve represents the supposed number of particles deposited on each cathode and the curves have been dawn so that there are 1000 more square divisions under curve I, for the large voltameter, than under curve II, for the small voltameter. Each division, therefore, represents 10^9 particles. The rate at which the particles deposit is initially greater in the small voltameter, because the electric intensity at the cathode is greater, due to the smaller area, but as the available supply of particles is more limited than in the larger size, the curve falls off more rapidly, and at the end of the experiment the total number of particles deposited in the large voltameter is greater than in the small one.

In our earlier work[25] we showed that a contaminated solution, giving initially a strongly striated deposit, became purer as the electrolysis proceeded, until in the end the deposit was a normal crystalline deposit such as we always find from a pure electrolyte.

We think that the foregoing explanation of the volume effect is in accord with all the experimental facts and that it is a reasonable and logical explanation. It shows that using the same cathodes and anodes and porous cups the volume effect may be made to appear or disappear according as the electrolyte is contaminated or not, and that using the same cathode and solution the volume effect may be increased by increasing the volume of electrolytes (that is, increasing the amount of colloid present) as is done when the siphon voltameters are used. The theory of Richards and Anderegg,[26] assuming the effect to be a matter of greater inclusions on a greater cathode area, will explain neither of the above facts. But these facts have been demonstrated over and over again in our work. Our theory of the volume effect also shows that it is not a phenomenon of the porous-cup voltameter alone, as stated by von Steinwehr,[27] but is common to all forms. The diagrams which we have given above show that this is the case.

One further experiment was, however, tried to answer the question of whether the relatively dilute solution at the cathode surface could produce a false weight of deposit by unloading silver chloride, since it is well known that silver chloride is more soluble in strong silver-nitrate solutions than in weak ones. This has been clearly shown in a quantitative way recently by Lowry.[28] Accordingly, we prepared a 10 per cent solution of silver nitrate and saturated one portion of it with silver chloride, allowing the finely suspended particles to settle out during 48 hours, when the clear, supernatant liquid was decanted without filtration and electrolyzed in a large and small voltameter simultaneously with the portion not containing the silver chloride. No differences due to the chloride were found.

We believe that a careful study of the above data, giving the results of a large number of experiments, will lead to the conclusion that the reality and significance of the volume effect have been proved beyond question, and that it is a valuable criterion of the purity of the electrolyte.

WASHINGTON, March 28, 1916.

---

[25] This Bulletin, 9, p. 512.

[26] Loc. cit.

[27] Loc. cit.

[28] Proc. R. S., 91, p. 53; 1914.

CONSTANTS OF SPECTRAL RADIATION OF A UNIFORMLY HEATED INCLOSURE OR SO-CALLED BLACK BODY, II

By W. W. Coblentz

CONTENTS

Page

I. Introduction 459

II. Recomputation of data 461

III. Discussion of other data 468

IV. Summary 470

Appendix—Note on methods of calculating the spectral radiation constants 471

I. INTRODUCTION

In a previous communication[1] the results of an investigation of the constant of spectral radiation of a black body were presented. The spectral energy curves were obtained by means of a vacuum bolometer, a mirror spectrometer, and a perfectly clear fluorite prism.

In the isothermal spectral energy curves obtained with these instruments the position λ_m of the maximum emission E_m, was computed by taking the wave lengths, λ_1 and λ_2, corresponding to equal intensities, $E_{\lambda_1} = E_{\lambda_2}$, on the assumption that the observed energy curve fits the Planck equation. The equation which is used in computing λ_m is

$$\lambda_m = \frac{\alpha\ (\log\lambda_2 - \log\lambda_1)\lambda_1\lambda_2}{\alpha'(\lambda_2 - \lambda_1)\log e} - \frac{\lambda_1\lambda_2[\log(1 - e^{-c/\lambda_1 T}) - \log(1 - e^{-c/\lambda_2 T})]}{a'\ (\lambda_2 - \lambda_1)\log e}$$

The second term in this equation is rather complicated. It requires an approximate value of the spectral radiation constant, C, which was assumed, for the purpose of calculating this correction (for the series of 1909 to 1911), to be $C = 14\,500$. A decrease of 100 units in C (say $C = 14\,400$) decreases the mean value[2] of λ_m by 0.0012μ, which at that time was considered negligible.

---

[1] This Bulletin, 10, p. 2; 1913.

[2] In the previous paper this value was stated to be 0.005μ, which is erroneous.

The second term in the above equation, which is usually mentioned as a "correction factor" has always been a stumbling block in the computations. After the completion of the calculations of λ_m it was found that the computer had omitted a factor from this "second term" which introduced an error of about 0.5 per cent, giving a mean value of $C = 14\,280$ (0.5 per cent too low).

Some doubts arose also as to the accuracy of part of the calibration curve of the prism, known as the "calibration curve of 1912," in view of the general belief, held at that time, that the value can not be lower than $C = 14\,500$. To save work in correcting this error in the "second term," fewer points were taken, and the values of λ_2, at 4 to 5μ, were increased by a slight amount to correspond with the "calibration curve of 1910." The data thus obtained gave a mean value of $C = 14\,456$, which is about 0.2 per cent higher than would have been obtained by adhering to the "calibration curve of 1912," published in the previous paper.

These data were published in 1913, the intention being to revise them, if the calibration curve of 1910 should be found wrong. In the meantime Paschen[8] has published further data on the dispersion of fluorite which shows that the part of the calibration curve of 1910, used by the writer in the above computations, is less reliable than the calibration curve of 1912.

Recently, on examining the previous computations, it was found that the above-mentioned "second term" still contains a small error, giving a mean value of λ_m, which is 0.2 to 0.3 per cent too high. As a result of these errors, which happen to be of the same sign, the value of $C = 14\,456$, previously published, is 0.5 to 0.6 per cent too large, owing to faults in the calibration curve and to a small error in the reduction of the data.

The computations have therefore been made anew, using the values of λ_1 and λ_2 which had been read from the spectral energy curves obtained with the prism calibration curve of 1912. The recomputation of these data turned out to be a simple matter, in view of the fact that it merely required dividing the above-mentioned "second term" factors by 2.3 and subtracting 0.0038μ from the mean value of λ_m. The subtraction of 0.0038μ is necessary because C = 14 600 instead of C = 14 300 had been used in computing the second-term factors of the "data of 1912."

---

[8] Paschen., Ann. der Phys., **41**, p. 670; 1913.

The difficulty encountered in this investigation was an overabundance of spectral energy curves, the viewing of which caused such fatigue to the eyes that, after having drawn the curves and indicated the best positions for obtaining λ_1 and λ_2, it was necessary to assign to another the task of reading off the numerical values of λ_1 and λ_2 from the curves and computing the results. After a lapse of more than three years the writer finds no corrections to the values of λ_1 and λ_2 as then read from the energy curves by his assistant, showing that the work had been faithfully done. As for the errors in the computations, owing to eye fatigue, it was impossible for months thereafter to give attention to the reduction of the data. Furthermore, at that time a correction of 0.3 to 0.5 per cent was considered of minor importance in view of the great difficulties involved in the work. It is of interest to note that the discrepancies in the previous paper are due to faults in reduction of the data and not in the experimental work. The present disagreement between theory and experiment is very small, and may be further reduced when we know more about the optical constants of the prism used in producing the spectrum.

II. RECOMPUTATION OF DATA

As already mentioned, the recomputation of the data consisted simply in eliminating the errors in the "second-term correction" which is used in obtaining λ_m. The total number of points on the energy curve was usually greatly increased. In this manner a mean value of λ_m was obtained which is more representative of the whole energy curve. The values of λ_2 were taken in the regions where there is no atmospheric absorption, viz, 2.3 to 2.5μ, 3.3 to 4.1μ, 4.4 to 4.6μ, and 4.8 to 5.6μ. In the previous paper the value of C was based upon data obtained in 1911 and the "series of 1912." The "series of 1911" contained many curves taken at extreme temperatures. For the low temperatures the curves were greatly affected by atmospheric absorption, and at high temperatures the scale of temperatures was questioned. Correcting these data a mean value of $C = 14\,390$ was obtained for the "series of 1911." However, considering the quality of the spectral energy curves, it does not seem fair to give them any weight in deducing a new mean value, although it would increase the corrected mean value but little.

As mentioned in the previous paper the "series of 1912" observations are considered the most accurate (1) as regards adjustments of apparatus, (2) temperature scale, (3) bolometric control, (4) elimination of atmospheric water vapor, and (5) as regards the general appearance of the spectral energy curves. These data were therefore carefully recomputed and tabulated. In making up the tables the column of probable errors is omitted in view of the writer's feeling that such data are illusory.

In the present paper the old numbers of the tables are carried in a footnote at the end of each table to facilitate comparison with the data in the previous paper to which reference must be made for details. Series 8, Table 6, is poor owing to various difficulties that were experienced—that is, tremors, bolometric troubles, etc.—so that only the most reliable curves were considered in the present computations.

TABLE 1[a]

Series 1912, I.—White Radiating Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2.

[Energy curves LXXXVI-XCII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})				$\lambda_{max}T$		$C = \alpha\lambda_{max}T$	
			Mean value		Number of computations		Old	New	Old	New
			Old	New	Old	New				
		°	μ	μ						
XCIII[b]	?	1112	2.605	2.601	3	3	2922	2897	14 508	14 384
LXXXVIII	P	1209	2.408	2.401	6	6	2910	2903	14 451	14 414
XCI[b]	P	1223	2.374	2.356	4	7	2904	2881	14 418	14 304
LXXXVII	PW	1242	2.345	2.332	5	9	2912	2896	14 459	14 379
LXXXVI	P	1350	2.154	2.139	6	7	2908	2888	14 438	14 339
LXXXIX[c]	P	1419	2.056	2.034	7	7	2916	2886	14 480	14 329
XC[b]	PW	1427	2.045	2.031	5	3	2918	2898	14 486	14 389
Mean							2913	2892	14 463	14 362

[a] Table 12 of previous paper.

[b] Furnace heated by outer coil only.

[c] Poor curve.

TABLE 2[a]

Series 1912, II.—Black (Cr_2O_3) Radiating Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy curves, XCIII–CVI]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})				$\lambda_{max}T$		$C=\alpha\lambda_{max}T$	
			Mean value		Number of computations		Old	New	Old	New
			Old	New	Old	New				
		°	μ	μ						
CVI[b]	P	1025	2.824	2.817	5	5	2895	2887	14 372	14 334
XCIX	P	1153	2.507	2.496	4	6	2891	2878	14 356	14 289
XCVIII[b]	P	1223	2.375	2.343	4	7	2904	2866	14 419	14 230
XCVII	P	1301	2.226	2.209	6	8	2896	2874	14 379	14 270
CV	P	1338	2.183	2.151	5	6	2921	2878	14 503	14 289
XCV[b]	P	1351	2.145	2.127	4	7	2898	2874	14 388	14 270
XCVI	P	1377	2.104	2.092	4	8	2897	2881	14 385	14 304
CIV	P	1401	2.080	2.059	6	8	2914	2885	14 470	14 324
XCIV	P	1420	2.050	2.026	7	9	2909	2877	14 442	14 285
CII	P	1453	2.003	1.992	7	9	2910	2894	14 450	14 368
CIII	P	1479	1.973	1.947	5	5	2918	2879	14 491	14 295
XCIII	P	1501	1.944	1.918	4	7	2917	2879	14 485	14 295
CI	PW	1525	1.908	1.893	5	8	2910	2877	14 447	14 334
C	P	1687	1.726	1.717	5	5	2912	2896	14 457	14 378
Mean							2907	2881	14 432	14 303

[a] Table 13 of previous paper.

[b] Poor curves.

TABLE 3[a]

Series 1912, III.—New Radiator, White Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy curves, CVII–CXIII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})				$\lambda_{max}T$		$C=\alpha\lambda_{max}T$	
			Mean value		Number of computations		Old	New	Old	New
			Old	New	Old	New				
		°	μ	μ						
CXIII[b]	?	1151?	2.540		3		2921		14 504	
CX	PW	1223	2.383	2.373	6	5	2914	2902	14 469	14 408
CXII	P	1276	2.275	2.264	6	9	2903	2889	14 412	14 344
CIX	P?	1352	2.155	2.142	7	7	2914	2896	14 466	14 379
CXI	P	1379	2.109	2.101	5	7	2911	2897	14 451	14 384
CVIII	P	1453	2.003	1.996	5	5	2910	2900	14 450	14 398
CVII	P	1527	1.913	1.886	4	5	2921	2880	14 508	14 299
Mean							2913	2894	14 466	14 368

[a] Table 14 of previous paper.

[b] Poor curve.

TABLE 4[a]

Series 1912, IV.—New Radiator, Black ($Cr_2O_3+2Co_2O_3$) Walls, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy curves, CXIV–CXXIII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})				$\lambda_{max}T$		$C=\alpha\lambda_{max}T$	
			Mean value		Number of computations		Old	New	Old	New
			Old	New	Old	New				
		°	μ	μ						
CXXIII[b]	P?	876	3.312	3.280	3	5	2901	2873	14 405	14 265
CXXII	P	1025	2.826	2.818	8	9	2897	2888	14 382	14 339
CXXI	P	1077	2.704	2.694	5	6	2912	2901	14 459	14 404
CXVIII	P	1154	2.516	2.507	6	7	2903	2893	14 414	14 364
CXX	PW	1223	2.376	2.364	5	9	2906	2891	14 428	14 354
CXVII	P	1276	2.280	2.270	5	5	2909	2896	14 445	14 379
CXIX	P	1353	2.156	2.139	6	7	2917	2894	14 486	14 369
CXVI[b]	P	1377	2.122	2.104	6	3	2922	2897	14 507	14 384
CXV	P	1454	2.007	1.996	6	6	2918	2902	14 488	14 408
CXIV[b]	P	1503?	1.954	....	4	....	2936	....	14 580?	....
Mean	....	....	....	....	....	....	2910	2893	14 446	14 363

[a] Table 15 of previous paper. [b] Poor curves.

TABLE 5[a]

Series 1912, V.—Blackened Radiator, New Adjustments, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy curves, CXXIV–CXL]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})				$\lambda_{max}T$		$C=\alpha\lambda_{max}T$	
			Mean value		Number of computations		Old	New	Old	New
			Old	New	Old	New				
		°	μ	μ						
CXXXV[b]	?	1026	2.831	2.822	5	5	2905	2895	14 423	14 374
CXXXII[b]	P	1077	2.703	2.692	5	7	2911	2899	14 455	14 394
CXXXIV	PW	1153	2.520	2.509	6	7	2905	2893	14 425	14 364
CXXXI	P	1194	2.441	2.433	4	6	2914	2905	14 469	14 424
CXXIX	P	1224	2.380	2.368	6	6	2913	2898	14 464	14 389
CXXVI	P+	1276	2.284	2.271	9	6	2914	2898	14 469	14 389
CXXXIII	P+	1302	2.237	2.226	6	6	2913	2898	14 461	14 389
CXXXVII	PW	1302	2.242	2.231	7	6	2920	2904	14 498	14 419
CXXX	P	1338	2.182	2.164	5	5	2920	2895	14 497	14 374
CXXVIII	P+	1352	2.160	2.136	4	4	2921	2888	14 501	14 339
CXXV	P	1378	2.118	2.096	5	8	2918	2888	14 483	14 339
CXXXVI	P	1421?	2.068	....	5	....	2939	....	14 588?	....
CXXVII	P+	1454	2.008	1.996	9	5	2920	2902	14 497	14 408
CXXIV	P+	1503	1.961?	....	4	....	2948	....	14 629?	....
CXL[c]	P	1627?	1.798	1.794	5	....	2925	2919	14 524?	14 493?
CXXXVIII[c]	PW	1663	1.756	1.730	5	2	2921	2887	14 500	14 285
CXXXIX[b], [c]	P+	1796	1.639	1.615	8	5	2945	2900	14 631?	14 398
Mean	....	....	....	....	....	....	2915	2895	14 476	14 376

[a] Table 16 of previous paper. [b] Poor curves. [c] Alternating current used for furnace heating coils.

TABLE 6[a]

Series 1912, VIII.—Blackened Radiator, New Thermocouple, Fluorite Prism No. 1, Water-Cooled Shutter No. 2

[Energy curves, CLVI–CLXVII]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})				$\lambda_{max}T$		$C=\alpha\lambda_{max}T$	
			Mean value		Number of computations					
			Old	New	Old	New	Old	New	Old	New
		°	μ	μ						
CLIX[b]	?	806	3.610	....	....	....	2910	....	14 447	....
CLX	WP	879	3.300	3.286	2	7	2901	2888	14 402	14 339
CLXI[c]	P	953	3.052	3.039	2	7	2909	2896	14 441	14 339
CLVIII	P	1077	2.703	2.691	7	7	2911	2898	14 454	14 389
CLVII[d]	P?	1223	2.380	2.368	6	6	2911	2896	14 453	14 379
CLVI	P	1277	2.286	2.271	7	5	2920	2900	14 497	14 399
CLXIV[e]	P	1300	2.248	....	8	....	2923	....	14 513?	....
CLXVII[f, e]	WP	1314	2.236	....	7	....	2938?	....	14 588?	....
CLXIII	P	1376	2.120	2.103	6	3	2917	2894	14 482	14 369
CLXVI[c, e]	P	1377	2.140	....	5	....	2947?	....	14 634?	....
CLXII[g]	P+	1452	2.030	....	10	....	2948?	....	14 639?	....
CLXV[e, c]	P+	1539	1.920	....	9	....	2955?	....	14 671?	....
Mean	....	....	....	....	....	....	2912	2895	14 461	14 375

[a] Table 19 of previous paper.

[b] Very poor curve, λ max by inspection.

[c] Poor series, tremors.

[d] Poor curve.

[e] Radiation sensitivity changed.

[f] Furnace heated by outer coil only.

[g] Bolometer unsteady; low vacuum.

TABLE 7[a]

Series 1912, IX.—Blackened Radiator, Fluorite Prism No. 1, Water-Cooled Shutter No. 1

[Energy curves, CLXVIII–CLXXVI]

No.	Form of energy curve	Absolute temperature	Wave length of maximum emission (λ_{max})				$\lambda_{max}T$		$C=\alpha\lambda_{max}T$	
			Mean value		Number of computations					
			Old	New	Old	New	Old	New	Old	New
		°	μ	μ						
CLXXIV[b]	P?	1175	2.465	2.446	7	7	2896	2874	14 381	14 270
CLXXIII	P	1194	2.431	2.416	4	6	2900	2885	14 401	14 324
CLXXV	P	1277	2.272	2.257	5	6	2901	2882	14 405	14 309
CLXXII	P	1302	2.232	2.216	4	8	2906	2885	14 429	14 324
CLXXVI	P	1353	2.153	2.137	7	7	2913	2891	14 462	14 355
CLXXI	P	1377	2.114	2.101	7	5	2911	2893	14 456	14 365
CLXX	P	1451	2.010	1.996	7	8	2916	2896	14 477	14 379
CLXIX[b]	P	1452	2.007	1.986	2	7	2914	2884	14 467	14 319
CLXVIII[b]	P	1540	1.890	1.871	2	4	2909	2881	14 443	14 304
Mean	....	....	....	....	....	....	2909	2886	14 436	14 327

[a] Table 20 of previous paper.

[b] Poor curves, sensitivity changing.

TABLE 8

Reproductibility of Data Using Different Radiators

Date	Number	Absolute temperature °	λ_{max}	$\lambda_{max}T = 2890$	$\Delta\lambda_{max}T$	$C = \alpha\lambda_{max}T$
February 8, 1912	CVI	1025	2.817	2887	−3	14 334
February 20, 1912	CXXII	1025	2.818	2888	−2	14 339
February 17, 1912	CXVIII	1154	2.507	2893	+3	14 364
February 27, 1912	CXXXIV	1153	2.509	2893	+3	14 364
February 14, 1912	CXII	1276	2.264	2889	−1	14 344
February 17, 1912	CXVII	1276	2.270	2896	+6	14 379
January 29, 1912	LXXXVI	1350	2.139	2888	−2	14 339
February 13, 1912	CIX	1352	2.143	2896	+6	14 379
February 24, 1912	CXXVIII	1352	2.136	2888	−2	14 339
February 19, 1912	CXIX	1353	2.139	2894	+4	14 369
March 27, 1912	CLXXVI	1353	2.137	2891	+1	14 355
March 26, 1912	CLXXI	1377	2.101	2893	+3	14 365
February 23, 1912	CXXV	1378	2.096	2888	−2	14 339

TABLE 9[a]

Summary of Data Given in the Preceding Tables

Series	Number of energy curves	Mean value C		Remarks
		Old	New	
1911				
I	26	14 469	14 390	Unpainted Marquardt porcelain radiator. (Water-cooled shutter No. 2.)
1912				
I	7	14 463	14 362	Unpainted radiator as used in 1911.
II	14	14 432	14 303	Radiator painted with chromium oxide.
III	6	14 466	14 368	New unpainted Marquardt radiator.
IV	9	14 446	14 363	Radiator painted with a mixture of the oxides of cobalt and chromium.
V	14	14 476	14 376	Radiator repainted; optical path readjusted.
VIII	6	14 461	14 375	New thermocouples; radiator the same as in the preceding series.
IX	9	14 436	14 327	New water-cooled shutter, No. 1; the rest of the apparatus is the same as in the preceding series.

New mean value $C = 14\ 353$ (94 energy curves; 1912)
$A = 2891$

$\left.\begin{array}{l} C = 14369 \\ A = 2894 \end{array}\right\}$ Final value after applying all corrections

[a] Table 21 of previous paper.

That conditions were reproducible is indicated (Table 8) by the closeness in the agreement of the values of the radiation constant for various radiators heated to the same temperature. In only a few cases is the error greater than 1°, which is as close as the temperature scale was known at that time. In fact, considering the difficulties involved in making the measurements and the appearance of the spectral energy curves, it is surprising to find so close an agreement (the maximum range is only about 0.5 per cent) now that the computations have been made and the data assembled for inspection.

In Table 9 are assembled the reliable data which form the basis for obtaining a mean value of the radiation constants. The mean value of all the data including the "series of 1911" is $C = 14\,358$. However, as already stated, the data of 1911 are not as reliable as is desirable, and since there is no way of estimating their value the writer prefers to consider only the "series of 1912," which contains seven sets of observations (65 energy curves), which give a mean value of $C = 14\,353$ micron degrees and $A = 2891$ micron degrees.

If the corrections to the temperature scale (mentioned in the previous paper) are applied, the value is $C = 14\,362$. A further correction $(= +7)$ is necessary because the second term in equation 1 was computed using $C = 14\,300$ instead of $C = 14\,350$. Hence, the final corrected value is $C = 14\,369$ and $A = 2894$ micron degrees.

A recent investigation of instruments and methods for evaluating radiant energy in absolute value[4] gave a new determination of the coefficient, σ, of total radiation[5] of a black body. The numerical value as published is $\sigma = 5.72 \times 10^{-12}$ watt. cm.$^{-2}$ deg.$^{-4}$, which from our present knowledge appears to be close to the true value. Hence, if theoretical considerations are to be relied upon, this value of the coefficient, σ, of total radiation indicates that the coefficient of spectral radiation is of the order of $C = 14\,322$, as compared with the experimentally determined value $C = 14\,369$. This is a difference of only 0.3 per cent. The agreement is so close that it must be considered accidental in view of the great experimental difficulties involved in obtaining the data. These data were obtained at different dates, on the same radiator (operated under various conditions), and using the same scale of temperatures. The small outstanding discrepancy is probably as much the result of uncertainties in the calibration curve (refractive indices) of the fluorite prism as it is the result of uncertainties in the temperature scale, and of the inevitable experimental errors.

---

[4] This Bulletin, 12, p. 504; 1916.

[5] This Bulletin, 12, p. 553; 1916. The first issue gave a value of $\sigma = 5.75$, which is incorrect.

III. DISCUSSION OF OTHER DATA

Paschen's Data.—After a lapse of about 18 years it is interesting to turn back to the pioneering work of Paschen and observe how close he came to the truth.

In his first paper Paschen[6] used four radiators, heated to 100°, 191°, 304°, and 450°, respectively, and 4 bolometers. He obtained a series of closely agreeing values which gave a mean value (2894, 2892, 2888, 2890) of $\lambda_m T = 2891$. Using the Planck reduction factor (4.9651) instead of the Wien factor (5), this gives a value of $C = 14\,354$. The following year Paschen[7] obtained a series of spectral energy curves from radiators operated at high temperatures. He obtained a value of $A = 2921$ as a result of arbitrarily changing his calibration curve as described in the writer's previous paper. He changed also his previous data, increasing the value of A from 2891 to 2915, or about 0.9 per cent. From this it would appear that his later value ($A = 2921$) is 0.9 per cent higher than it should have been; that is, his experimental values were close to $A = 2895$ and $C = 14\,374$. In other words, Paschen's original data fall within the range of the recent and more accurately determined values.

The Reichsanstalt Data.—During the past 16 years the Phys.-Tech. Reichsanstalt, at Berlin, has pursued extensive investigations of the laws of radiation and their application to the temperature scale. The first investigation by Lummer and Pringsheim[8] gave a mean value of $A = 2879$. In their second paper they obtained a much higher value, viz, $A = 2940$.

In 1906 Holborn and Valentiner[9] obtained a value of $C = 14\,200$ as a result of a series of spectrophotometric measurements. This is now admittedly in error, owing to an erroneous temperature scale in which the melting point of palladium was taken to be 1575° instead of about 1550°. Recently Valentiner[10] corrected this value, raising it to $C = 14\,350$.

During the past seven years these investigations have been pursued by Warburg[11] and his collaborators. In their first communication[12] they reported a value of $C = 14\ 570$. They questioned the temperature scale and proceeded to make their investigations at high temperatures by using the radiation laws to establish their temperature scale, thus avoiding the temperature scale as transferred from the gas thermometer by means of thermocouples. They retain only one temperature fixed point, viz, gold at 1064° (later 1063°). The higher temperatures (1400°) were determined radiometrically.

---

[6] Paschen, Sitzber. Akad. Wiss., Berlin, **21**, p. 403; 1899.

[7] Paschen, Ann. der Phys., **4**, p. 277; 1901.

[8] Lummer and Pringsheim, Verh. Phys. Ges., **1**, pp. 23, 215; 1899.

[9] Holborn and Valentiner, Am. der Phys. (4), **22**, p. 1; 1906.

[10] Valentiner, Am. der Phys. (4), **29**, p. 489; 1912.

[11] (1) Warburg and Leithauser, Z. S. für Instrk., **30**, p. 118, 1910; (2) Warburg and Leithauser, Z. S. für Instrk., **31**, p. 124, 1911; (3) Warburg, Hupka, and Müller, Z. S. für Instrk., **32**, p. 134; 1912; (4) Warburg, Leithauser, Hupka, and Müller, Sitzer Akad, Wiss. Berlin I., p. 35, 1913; (5) Warburg, Leithauser, Hupka, and Müller, Ann. de Phys. (4), **40**, p. 609, 1913; (6) Hoffmann and Meissner, Z. S. Instrk., **33**, p. 157, 1913; (7) Warburg, Hupka, and Müller, Z. S. Instrk., **34**, p. 115, 1914; (8) Warburg and Müller, Z. S. Instrk., **35**, p. 98, 1915; (9) Warburg and Müller, Ann. der Phys., **48**, p. 410, 1915.

In their next communication (2) values are reported which varied from $C = 14\ 200$ to 14 600. In the following report (3) the fluorite prism gave values ranging from $C = 14\ 300$ to 14 600 and it was discarded. A quartz prism gave a value of $C = 14\ 360$; and in a more complete paper (4 and 5) the values of $C = 14\ 370$ and $A = 2894$ are given. These values have stood for some years. A subsidiary investigation (6) of the relative brightness of a black body at the melting point of palladium and of gold gave a value of $C = 14\ 440$.

Recently further data (8 and 9) were published, in which a value of $C = 14\ 250$ was obtained from the temperature scale based on the Stefan-Boltzmann law of total radiation and a value of $C = 14\ 300$ or 14 400 was obtained by using the Wien displacement law to establish the temperature. The uncertainty in the value of $C = 14\ 300$ or 14 400 is owing to the uncertainty in their calibration curve (refractive indices) of the quartz prism which is now being investigated. The present status is the adoption[13] of the value of $C = 14\ 300$, although from the reliability of Paschen's determinations of the refractive indices of quartz the chances are that the higher value ($C = 14\ 350$ to $C = 14\ 400$) may be found nearer the correct value.

In passing, it is of interest to note that their recent determinations of the absorption coefficients of quartz are in close agreement with those published by the writer,[14] excepting at 2.21 μ, where they find a narrow absorption band. Any errors made in eliminating the effect of this absorption upon the spectral energy curve will affect the temperature scale and hence indirectly the value of the spectral radiation constant.

From this brief review of the experimental data now available it appears that the value of the spectral radiation constant lies between $C = 14\ 300$ and $C = 14\ 400$.

---

[12] Sitzber., **44**, p. 225; 1910.

[13] Warburg, Verh. Phys. Ges., **18**, p. 1; January. 1916.

[14] This Bulletin, **11**, p. 471; 1914.

IV. SUMMARY

The present paper gives the result of a recomputation of the constants of spectral radiation of a black body, which had been published in a previous paper. This recomputation was necessitated as the result of the adoption of a new and apparently more reliable calibration curve of the fluorite prism used in the work, and as a result of the discovery of a small error which was found in the previous computations. Although these errors are small (and would have been considered negligible four years ago) they happen to be of the same sign and hence have an appreciable effect upon the final result.

The results of the present computations give a mean value of $C = 14\ 369$, which is close to the mean value of all the published data.

The data of other investigators are summarized and it is found that they lie close to $C = 14\ 350$.

From a consideration of the data now available it appears that the values of the constants of spectral radiation are close to

$$C = 14\ 350 \text{ micron degrees.}$$
$$A = 2890 \text{ micron degrees.}$$

and that the coefficient of total radiation is of the order of

$$\sigma = 5.7 \times 10^{-12} \text{ watt cm}^{-2} \text{ deg.}^{-4}$$

This indicates that the constant, h, of the quantum theory is of the order $h = 6.56$ to 6.57×10^{-27} erg sec.

WASHINGTON, March 24, 1916.

APPENDIX

NOTE ON METHODS OF CALCULATING THE SPECTRAL RADIATION CONSTANTS

Because of the difficulties involved in maintaining a vacuum bolometer at a constant radiation sensitivity or in determining its radiation sensitivity from day to day it has been the custom to observe isothermal spectral energy curves and compute the value of λ_m as an intermediary step in obtaining the value of the constant C.

In the work just described the radiation sensitivity of the vacuum bolometer was determined by using the black body as a standard of radiation. It was therefore not possible to compare data obtained on different days, although the black body served as a convenient standard of radiation for comparison while observing any one isothermal energy curve.

The difficulty in obtaining a value of the constant C by computation from observations on an isothermal spectral energy curve has always been due to the uncertainty as to what formula should be used. If the Wien equation is used, then $\alpha = 5$; and if the Planck equation is used, then $\alpha = 4.9651$.

In computing his values of λ_m Paschen used the Wien equation, although it did not fit his best data. This gave him a high value of C, as mentioned on a previous page, where a lower and more probable value is given.

From the very beginning of his investigations on black-body radiation the writer found that the Wien equation did not fit his spectral energy curves. The assumption was therefore tentatively made that the observed curves fit the Planck equation; and, at the completion of the investigation, this was found to be true for about 75 per cent of all the observed curves. This conclusion was based upon the uniformity of the values of λ_m which resulted from computation (by the method of equal ordinates $E_{\lambda_1} = E_{\lambda_2}$) of values of λ_1 and λ_2 which were taken far apart, and also close together, on the observed isothermal spectral energy curve.

The method of equal ordinates was used because in this manner it was possible to utilize values of λ_1 and λ_2 which correspond with values of E_{λ_1} and E_{λ_2} which are closely the same in magnitude as originally observed, and hence contain the same errors of observation;[15] also the slit widths are closely the same. This method does not require the most accurate wave lengths and refractive indices (at least not for values of λ_2 greater than 4.5 μ) and it permits the selection of parts of the spectral energy curves which are free from atmospheric absorption bands. This accounts for the uniformity of the values of the constant *C*, given on a preceding page, although from the irregular appearance of the complete curves this does not seem possible. (See Fig. 1.) At a temperature of 1000° C. and at $\lambda_2 = 4.5\mu$ to 6μ an error of $\lambda = 0.05\mu$ changes λ_m by 0.007μ to 0.008μ. This amounts to 0.7 per cent in the value of *C*, and is much greater than would occur in practice.

---

[15] The bolometer-galvanometer (zero reading) is always unsteady by 0.1 to 0.3 mm whether the deflection is 5 mm or 200 mm. Hence the parts of the curve having the same sized deflections have the same accuracy.

The data obtained by Warburg[16] and his collaborators were calculated by using $E_{\lambda 1}$, E_m, λ_1, and λ_m. This may introduce complications because E_m often occurs in the region of the spectrum where there are atmospheric absorption bands, and where the slit-width data are difficult to determine. The method requires a more accurate knowledge of the calibration of the prism and greater refinements in the observations. They found that, using a fluorite prism, the value of *C* computed by using λ_1 on the short wave-length side of λ_m was different from the value obtained by taking λ, on the long wave-length side of λ_m. In the second paper they report that when using a quartz prism (which has about three times the dispersion of fluorite and hence gives greater accuracy in wave lengths, spectral purity, etc.) this difficulty was not found. Of course, this test could not be made in the long wave lengths because of the opacity of the prism. However, it seems quite conclusive that the disagreement in the computations, when using the data obtained with a fluorite prism, is to be attributed to experimental errors rather than to failure of the Planck equation. The writer experienced this same difficulty when using this method of computation, and hence used the method of calculating the constants by taking equal ordinates on the isothermal spectral energy curve.

The method of equal ordinates necessitates reducing the prismatic spectral energy measurements to a normal spectrum, plotting the data upon coordinate paper and drawing in a smooth curve from which the values of λ_1 and λ_2 are read corresponding with the equal ordinates $E_{\lambda 1}$ and $E_{\lambda 2}$. Although it requires but little additional time to plot the data after having made the observations, if one is certain that the observations lie close to the curve, the obviously logical procedure is to compute the spectral radiation constants from any two observed points,[17] $E_{\lambda 1}$ and $E_{\lambda 2}$. This, however, does not shorten the observational work, for, as in previous investigations, it will be necessary to make observations at three adjacent spectrometer settings (separated by the width of the radiometer receiver) in order to determine the spectral purity factor which is required in order to reduce the data to a normal spectrum. After spending months in obtaining the data, the question of saving time in their reduction is of minor importance. It is desirable to draw the complete curve and preserve it for future reference. If the observations do not lie close to the smooth curve then this method is slightly arbitrary as to the manner of combining the observations so as to obtain an integration of the whole curve without making more computations than would be used in the "method of equal ordinates."

---

[16] Z. S. für Instr., **30**, p. 118, 1910; **31**, p. 124, 1911.

[17] Dellinger, Proc. Amer. Phys. Soc., Washington meeting, Apr. 21–22, 1916; this Bulletin, 1916.

The appropriate formula for computing the radiation constants from any two points on an isothermal spectral energy curve is easily deduced from Planck's equation, and in its complete form, as shown by Dr. Dellinger, is:

$$C = \frac{\lambda_1 \lambda_2 T}{(\lambda_2 - \lambda_1) \log e}\left[\log \frac{E_{\lambda_2}}{E_{\lambda_1}} + 5 \log \frac{\lambda_2}{\lambda_1} - \log \left(\frac{1 - e^{-c/\lambda_1 T}}{1 - e^{-c/\lambda_2 T}}\right)\right] \cdot \cdot \ (2)$$

The term "log $(1 - e^{-c/\lambda T})$" may be expanded into a series and usually all the factors can be neglected, except one which is log $e \cdot e^{-c/\lambda_2 T}$. It is therefore necessary to know the approximate value of C, as was required in the writer's [18] method of computation.

Dr. Dellinger has made computations on data observed by the writer, using values of E_{λ_1} and E_{λ_2}, which are on opposite sides of E_m, and which are closely the same in magnitude. He obtained values of λ_m, which are in very close agreement with the data obtained by the writer, who used the method of equal ordinates, $E_{\lambda_1} = E_{\lambda_2}$. However, when the computations were made for two points which are on the same side of the maximum and which do not lie close to the smooth curve drawn through all the observations, some of the values of λ_m are discordant, as observed by Warburg. This disagreement, however, was not systematic as observed by Warburg and it was not greater than the experimental errors (2 per cent) that may easily be present in the work. This may seem a little disconcerting to those not familiar with the difficulties in obtaining the observations. It is therefore relevant to say that because of the small dispersion, the large errors of observation, the uncertainties in the dispersion and in the slit-width factors, the possible presence of scattered radiation (which appears at 4.5μ to 5μ in the spectrum produced by a prism containing numerous cleavage surfaces), variations in temperature of the radiator, etc., the writer is of the opinion that the use of equal ordinates ($E_{\lambda_1} = E_{\lambda_2}$), or the use of the general solution of Planck's equation in which E_{λ_1} and E_{λ_2} are closely the same and on opposite sides of E_m, is the most satisfactory method of calculating the spectral radiation constants from isothermal spectral energy curves obtained with a fluorite prism. The general solution is probably a more sensitive test of the validity of Planck's equation, but it requires more accurate experimental data than the writer could obtain four years ago.

---

[18] This Bulletin, **10**, p. 7 (eq. 6); 1913.

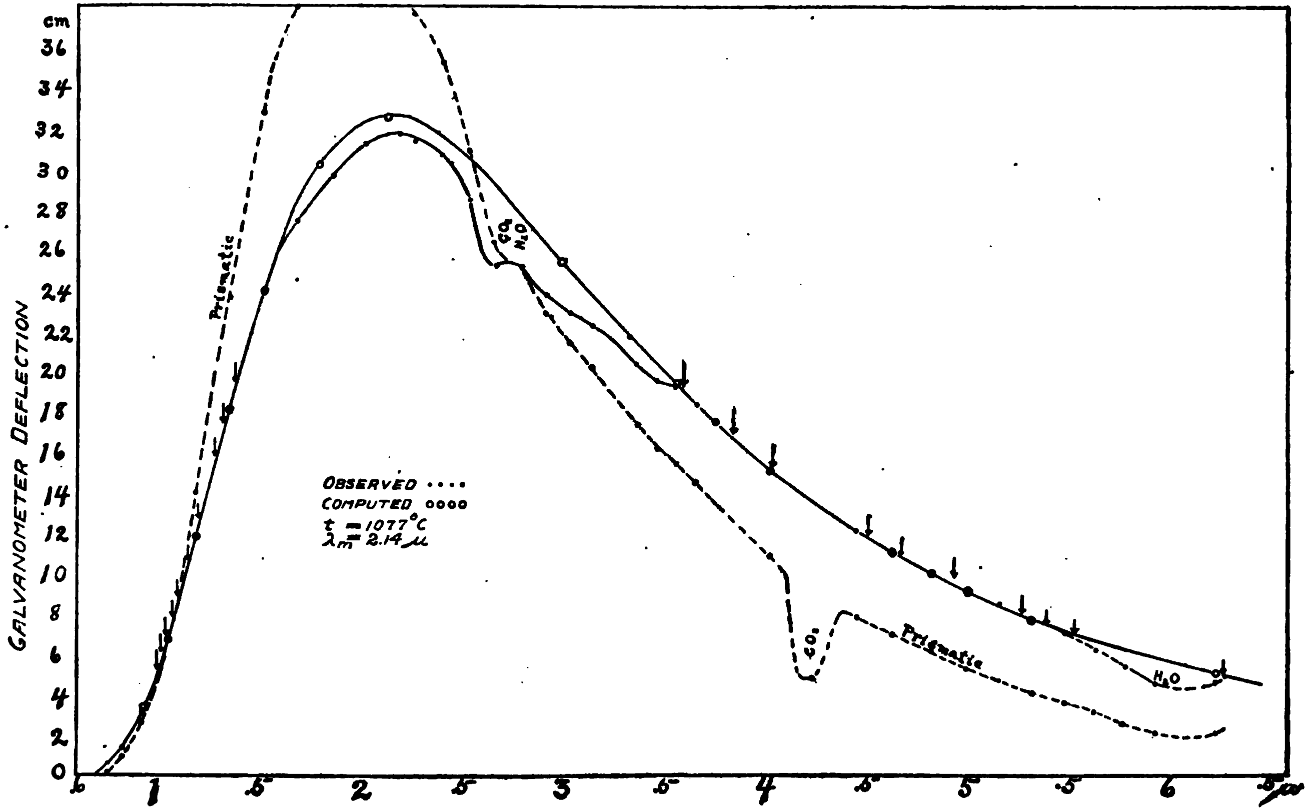


FIG. 1.—*Distribution of energy in the spectrum of a perfect radiator or so-called black body, observed with a vacuum bolometer, fluorite prism, and mirror spectrometer; also the theoretical curve*

In Fig. 1 is shown the observed spectral energy curve (in dotted lines; Series LXXXVI, 1912; see Table 1) of a black body at a temperature of 1077° C. The normal curve is shown by the continuous line. The arrows indicate points at which values of λ_1 and λ_2 were taken in order to compute λ_m by the method of equal ordinates.

This curve is typical of what was obtained when operating the radiator at 800° to 1000° C. From 1.7μ to 3.5μ the curve is irregular and often deeply indented, owing to atmospheric absorption bands of water vapor and carbon dioxide. Part of the indentation at 1.7μ might be caused by errors in the slit-width factors used for reducing the data to a normal spectrum and by absorption in the prism which, although quite free from color, belonged to the green variety of fluorite. An examination[19] of samples of lightly colored green fluorites showed small absorption bands at 1.6 to 3.5μ. Hence no attempt was made to obtain high accuracy in the observations extending from 2μ to 3μ, for it was not intended to use the data in the computations.

The absorption bands of atmospheric water vapor at 5.6μ to 6.2μ were also investigated.[20] At 6.25μ there is a narrow region of minimum absorption, amounting to 10 to 12 per cent, followed by absorption bands at 6.3 to 6.7μ.

In Fig. 1 the circles represent the computed emission, using Planck's equation and $C=14\,350$. In the region of the spectrum from 1μ to 1.6μ and from 3.6μ to 5.5μ there is a complete agreement between the observed and the computed curve. Several observed points deviate from the smooth curve by 1 to 2 per cent, which is better than one can expect, considering the fact that a correction had to be applied for a change in the radiation sensitivity of the bolometer.

An inspection of Fig. 1 and Eq. 2, shows that inconsistent values of C must result from combining data which are above and below the smooth curve and on the same side of λ_m. The computation by the method of equal ordinates suppresses these errors of observation by estimating the value of $E_{\lambda_1}=E_{\lambda_2}$ and by placing more of the burden of proof upon determinations of λ_1 and λ_2.

In obtaining the experimental data the usual procedure was to begin observations by making a few readings at a few points preceding the wave length (1μ in this series) at which computations were to be made. This was done for the purpose of "warming up the apparatus" and for obtaining the "purity factor" to reduce the data to a normal spectrum. Only three readings were made at 0.92μ, and the temperature of the radiator had not yet become steady. Hence, the writer does not consider the small difference between the observed and the computed value at 0.92μ to be due to a real disagreement between theory and experiment. The same is true for the region of the spectrum beyond 6μ. Correcting for atmospheric absorption at 6.24μ produces exact coincidence between the observed and the computed values. When one considers that an accuracy higher than 1 per cent was difficult to attain, and that momentary disturbances might introduce a range of 2 to 5 per cent in the galvanometer readings which were less than 2 cm deflection, it is safe to say that the Planck equation fits the experimental data to 6.5μ.

---

[19] This Bulletin, 9, p. 116, Fig. 12.

[20] This Bulletin, 7, p. 635, Fig. 3.

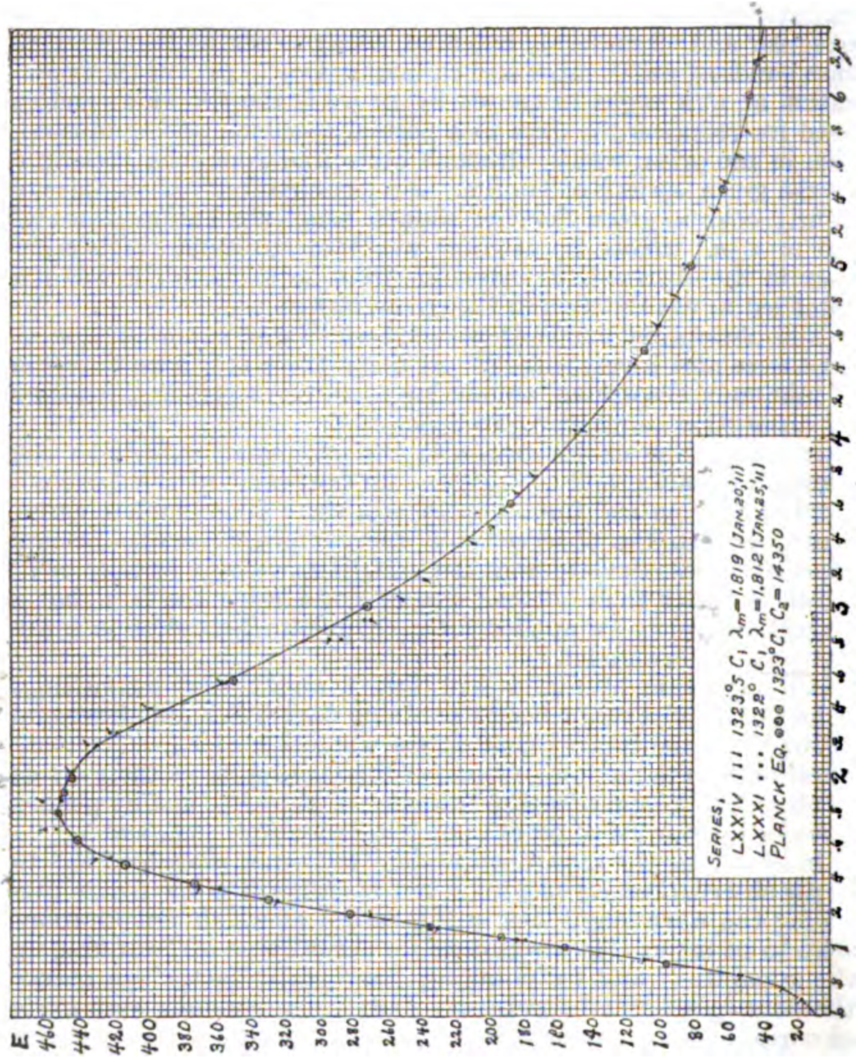


FIG. 2.—*Observed and computed energy distribution in the spectrum of a black body*

In Fig. 2 is shown the spectral energy distribution at 1323° C. It is typical of the curves obtained at high temperatures. This illustration gives two series of measurements obtained at different dates. The theoretical curve for $T = 1596°$ K and $C = 14350$ coincides remarkably well with the observations, considering the possibility of stray light, especially at 5μ where the observations are high. The low values at 0.7μ to 1μ, in Figs. 1 and 2, may be due to improper correction of the absorption by the silver mirrors. The slight shearing of the observed and the computed curves may be due to incorrect temperatures. At any rate it is hardly sufficient to be considered a real departure from the Planck equation; although as mentioned in the previous paper there are some indications that the Planck equation may not fit the observations beyond 7μ.

As mentioned in the previous paper, these data are the first indication that Planck's equation fits the experimental observations in this region of the spectrum. The few discordant experimental data obtained with optical pyrometers are hardly convincing proof that this equation does not apply also to measurements made in the visible spectrum. To make the test more conclusive, an outfit is being constructed for operating the radiator, and spectroradiometric apparatus in a vacuum, in order to eliminate atmospheric absorption. Because of the numerous subsidiary investigations which must be made preliminary to this investigation, some time must necessarily elapse before data can be obtained using all the apparatus in a vacuum.

SUMMARY OF EXPERIMENTS ON THE SILVER VOLTAMETER AT THE BUREAU OF STANDARDS AND PROPOSED SPECIFICATIONS

By E. B. Rosa and G. W. Vinal

CONTENTS

Page
I. Introduction 479
II. Literature of the voltameter.. 482
III. Summary of the voltameter work at the Bureau of Standards............ 485
IV. Specifications for the silver voltameter.................................. 497
  1. Previous specifications.. 497
  2. Specifications proposed by the Bureau of Standards............ 499
  3. Supplementary notes.. 501
Appendixes.. 507
  Appendix A.—Bibliography of the silver voltameter, with a few papers on closely allied subjects.. 507
  Appendix B.—Errata to the preceding papers.. 513

I. INTRODUCTION

The investigation of the silver voltameter at this Bureau was first begun by the late Dr. K. E. Guthe in 1904. His results were published in two papers[1] about a year later. The work was taken up again at the Bureau in 1907, when Dr. N. E. Dorsey, in cooperation with the present authors, began what was intended to be a short series of determinations to accompany the absolute measurements of current with the Rayleigh balance, which was then under construction. The results obtained at this time did not altogether confirm the experiments of the National Physical Laboratory which were then newly published, and new difficulties arose which were not understood. These experiments were not published.

In the following year the work was resumed and preparations for a very thorough study of the silver voltameter were made. The voltameter received added importance when the ampere was adopted by the London Electrical Congress as the second fundamental electrical unit, so that the investigations which the present authors began in the summer of 1908 have passed beyond the original plans in scope and duration. This has also been due in large measure to the numerous and intricate sources of error which were discovered in the course of the work, all of which required painstaking investigation.

---

[1] This Bulletin, 1, pp. 21, 349.

Several photographs of the laboratories devoted to the voltameter work are of interest as a matter of record. Fig. 1 shows part of the voltameter laboratory during the time that the work of Parts I to IV and the comparison of the silver and iodine voltameters was in progress. The apparatus for controlling the current and measuring the time are clearly shown, as well as the voltameters themselves. Another view of this same room which, however, does not show much of the apparatus was published in the paper on the comparison of the silver and iodine voltameters (vol. 10, p. 427). Figs. 2 and 3 show the new voltameter laboratory (except the chemical laboratory). This was equipped with the same apparatus brought from the old laboratory when the electrical division of the Bureau moved into its new building. Fig. 3 shows the entrance to the constant temperature balance room. The balances were read by the telescopes and scales which are seen at the windows on either side of the door. In this new laboratory the experiments on inclusions in the silver deposits were made, and also some experiments for the paper on the volume effect. In addition to this suite of rooms, a small chemical laboratory completely equipped was reserved for the preparation and testing of the silver nitrate.

Other experimenters have cooperated with the present authors during the last seven and one-half years, and their names appear on the various publications in which they were particularly concerned. First of these was Dr. A. S. McDaniel, who joined us in July, 1909, to study the effects of filter paper on silver-nitrate solutions and to devise means for the purification and testing of silver-nitrate solutions. He also investigated a number of other chemical questions which arose during the time he was a member of the Bureau staff. Dr. McDaniel resigned from the Bureau in March, 1913. A few months later Dr. S. J. Bates, who was research associate in chemistry at the University of Illinois, came to the Bureau to conduct experiments on the iodine voltameter operated in series with the silver voltameter. The result of this work was to establish with greater precision than before the value

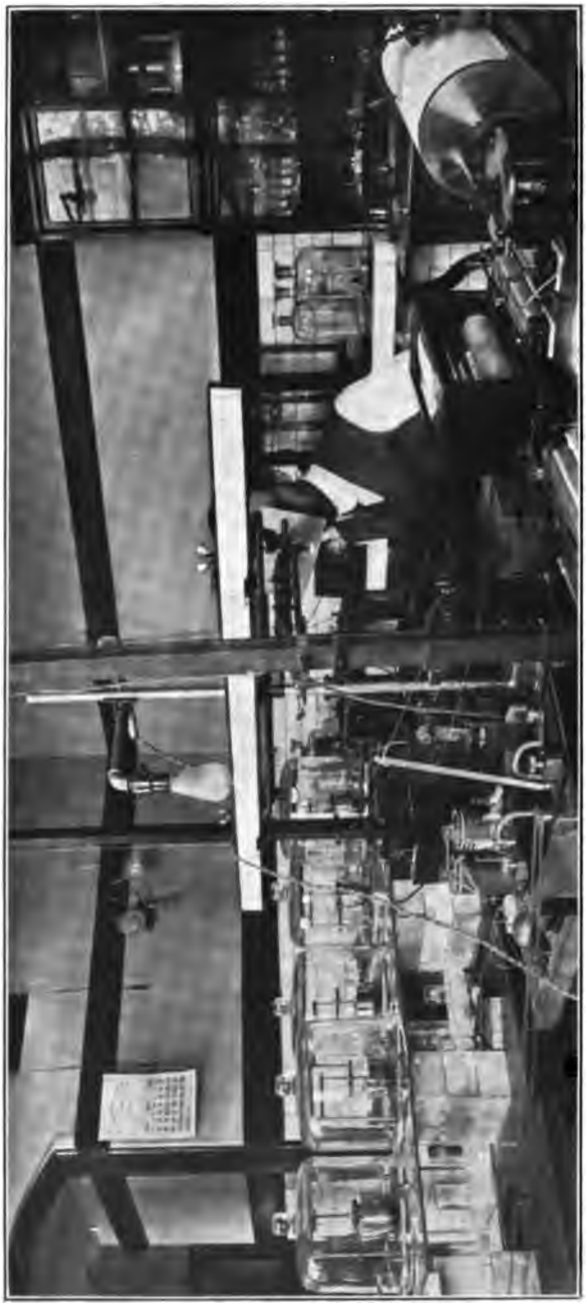


FIG. 1.—*The voltameter laboratory at the time of the International Committee experiments of 1910 and the work of Parts I to IV and the comparison of the Silver and Iodine Voltameters*

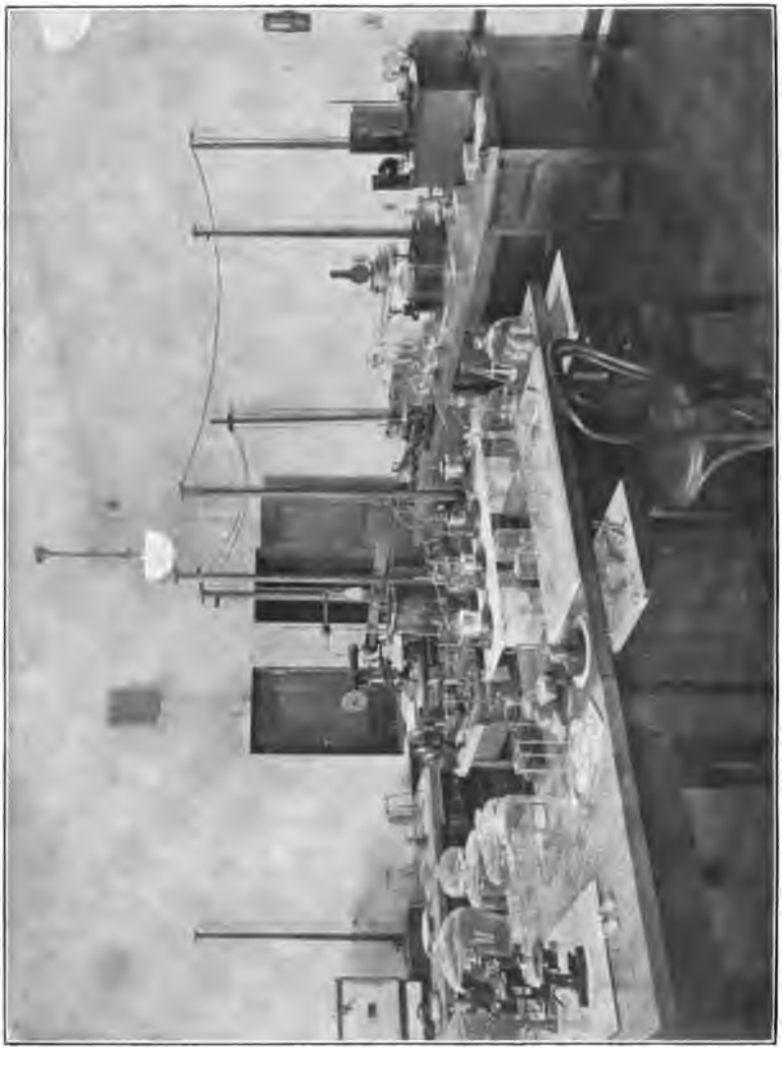


FIG. 2.—*The new voltameter laboratory, first used in 1915 for the experiments on "Inclusions in the Silver Voltameter Deposits" and the "Volume Effect"*

96 500 coulombs as the value of the Faraday. For five months in the early part of 1914 we cooperated with Prof. G. A. Hulett, professor of physical chemistry in Princeton University, in making joint comparisons of methods and materials for the silver voltameter, during which a previously neglected source of error in washing the deposits was discovered. Lastly, William M. Bovard, assistant in chemistry in Princeton, has collaborated at the Bureau in a determination of the foreign material included in the silver deposits.

It seems desirable at the present time to summarize the investigations that have been in progress at the Bureau since 1908 in order that the results of these experiments may be put forward with our proposed specifications for the silver voltameter as a measurer of electric current. Accordingly, in the present paper we present a résumé of the preceding papers which are listed below, and a specification for work of the highest precision with the silver voltameter which embodies the results of these investigations.

The present investigations of the voltameters have been published in the following papers:

The Silver Voltameter:

Part I, First Series of Quantitative Experiments, by E. B. Rosa and G. W. Vinal. This Bulletin, **9**, p. 151 (Reprint No. 194).

Extended abstracts in J. Wash. Acad. Sci., **2**, p. 451, 1912; Elec. World, **60**, p. 1261, 1912; Elektrotech. Zs., **34**, p. 232, 1913.

Part II, Chemistry of the Filter-Paper Voltameter and the Explanation of Striations, by E. B. Rosa, G. W. Vinal, and A. S. McDaniel. This Bulletin, **9**, p. 209 (Reprint No. 195).

Extended abstracts in J. Wash. Acad. Sci., **2**, p. 509, 1912; Elec. World, **60**, p. 1262, 1912; Elektrotech. Zs., **34**, p. 233, 1913.

Part III, Second Series of Quantitative Experiments and the Preparation and Testing of Silver Nitrate, by E. B. Rosa, G. W. Vinal, and A. S. McDaniel. This Bulletin, **9**, p. 493 (Reprint No. 201).

Extended abstracts in J. Wash. Acad. Sci., **3**, p. 40, 1913; Elec. World, **61**, p. 84, 1913; Elektrotech. Zs., **34**, p. 1168, 1913.

Part IV, Third Series of Quantitative Experiments and Special Investigations, by E. B. Rosa, G. W. Vinal, and A. S. McDaniel. This Bulletin, **10**, p. 475 (Reprint No. 220).

Extended abstracts in J. Wash. Acad. Sci., **4**, p. 52, 1914; Elec. World, **63**, p. 373, 1914; Elektrotech. Zs., **35**, p. 789, 1914.

Comparison of the Silver and Iodine Voltameters and the Determination of the Value of the Faraday, by G. W. Vinal and S. J. Bates. This Bulletin, **10**, p. 425 (Reprint No. 218); J. Am. Chem. Soc., **36**, p. 916, 1914.

Extended abstract in J. Wash. Acad. Sci., **4**, p. 69, 1914.

Studies on the Silver Voltameter, by G. A. Hulett and G. W. Vinal. This Bulletin, **11**, p. 553 (Reprint No. 240); J. Phys. Chem., **19**, p. 173, 1915.

Extended abstract in J. Wash. Acad. Sci., **4**, p. 593, 1914.

Inclusions in the Silver Voltameter Deposits, by G. W. Vinal and W. M. Bovard. This Bulletin, **13**, p. 147 (Reprint No. 271); J. Am. Chem. Soc., **38**, p. 496, 1916.

The Volume Effect in the Silver Voltameter, by E. B. Rosa and G. W. Vinal. This Bulletin, **13**, p. 447 (Reprint No. 283).

II. LITERATURE OF THE VOLTAMETER

In our first paper we gave a brief review of about 60 of the principal papers dealing with the silver voltameter, and in our later publications we have discussed some papers that have appeared since. There are, however, a considerable number of papers that have not been mentioned. A few of these are referred to below, but in an appendix a list is given of references dealing with the voltameter, which includes the papers previously discussed and a considerable number of other references. This list is possibly not complete, but it is believed that it includes practically all papers which report the results of investigations on the silver voltameter as an instrument of precision. It also includes many papers in which the voltameter was used simply to measure the quantity of electricity passing through the circuit and some references dealing with the various forms in which silver is deposited by the electric current, etc.

A very old paper which has recently come to our attention is interesting enough to call for brief notice here. It is by William Sturgeon,[2] who was sometimes inclined to be a severe critic of Faraday and his experiments. In view of the present universal acceptance of Faraday's laws of electrolysis and the use of the voltameter principle for a primary electrical standard it is somewhat amusing to read Sturgeon's views of Faraday's voltameter, as follows:

> The instrument certainly measures the gases liberated by the electric current, especially the hydrogen when collected separately, and in that capacity becomes an electrogasometer; but it has no pretensions whatever to the dignified rank of a measure of either the absolute or relative quantities of the electric matter transmitted. The idea of its indicating the extent of action in the voltaic battery would be perfectly absurd.

In 1911 Prof. Egoroff[3] published a preliminary account of the work which was being done on the electrical units at the Russian laboratory. This included experiments on the silver voltameter of the form designed by F. E. Smith, but no quantitative experiments are recorded since the work was interrupted by the death of M. Lebedev. These experiments have now been continued by

---

[2] Sturgeon's Annals of Electr., 1, p. 369; 1836.

[3] Report of Bu. of Wts. and Meas., Petrograd, p. 122; 1911.

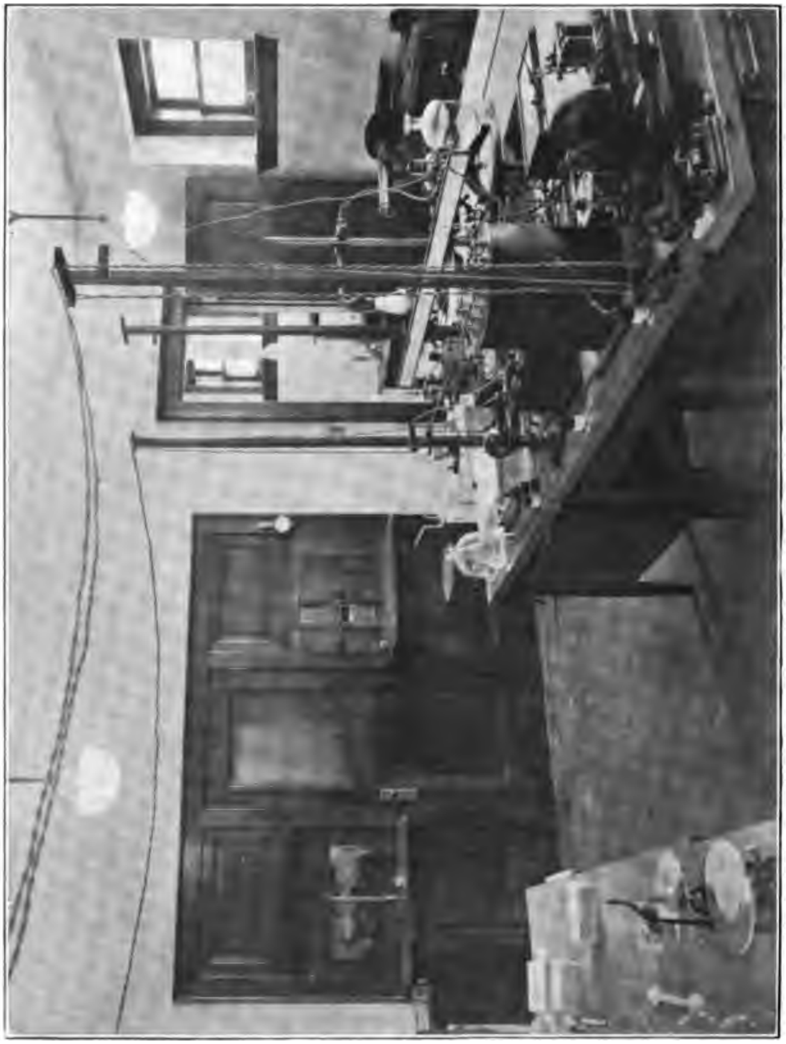


FIG. 3.—*The new voltameter laboratory, showing entrance to the balance room. The three balances are read by scales seen at the windows of the balance room and telescopes which project through the partition*

Mlle. Ferringer.[4] She has determined the voltage of some of the Weston cells prepared for the Russian Bureau of Weights and Measures. Four determinations with the voltameter of cell E average very nearly 1.01830.

Boltzmann [5] published in 1912 an account of his careful researches on the voltameter. He made tests for inclusions in his deposits by the method of heating the cups and deposits to a high temperature. Without mentioning the formation of platinum black in this process, the precautions which he took in preparing the cups probably eliminated this as a source of error in determining the inclusions. The results which have been recently obtained at this Bureau are in substantial agreement with Boltzmann's determinations of the inclusions.[6] He found a slightly greater deposit of silver when the deposits were made on a previous deposit than when they were made on the bare platinum. The results led him to conclude that this was due to an initial deposition of hydrogen on the bare platinum. We think this conclusion correct, but probably it occurs only under special conditions. We made special experiments [7] to determine the possibility of the deposit being diminished by an initial deposition of hydrogen ions on the ordinary platinum cups and found that this was not the case. The recent work done here on the matter of inclusions will, however, afford a ready explanation of the phenomenon observed by Boltzmann. We may reasonably assume that his cups after heating to redness contained a slight alloy of silver and platinum which would leave a thin layer of platinum black when the silver was removed. Boltzmann tells us that he glowed the cups before making the next deposit and this would convert the platinum black to platinum gray. The platinum gray, as we have shown, does cause a diminution of the deposit, probably owing to its catalytic action on the hydrogen ions. The important point here, however, is that Boltzmann's explanation holds, in our opinion, only when the cup contains platinum gray, which is an abnormal condition. He made experiments on the anode liquid and found it without effect on the cathode deposit. He also made experiments on the effect of light on the voltameter, with negative results.

Haga and Boerema [8] made a careful determination of the voltage of the Weston normal cell, using a tangent galvanometer, and in addition made determinations with the silver voltameter, finding 1.01826 international volts at 20° C for the cell and 1.11802 mg per coulomb for the absolute electrochemical equivalent of silver. These are in excellent agreement with the values found by ourselves.[9]

---

[4] Electritchestvo, 35.13, p. 260; 1914.

[5] Sitzber. Akad. Wiss. Wein, II A, 121, p. 1051.

[6] This Bulletin, 18, p. 161 (Reprint No. 271).

[7] This Bulletin, 10, p. 507 (Reprint No. 220).

[8] Arch. Neer. Sci. 8, p. 324; 1913.

Cohen [10] investigated the validity of Faraday's first law at high pressures. He arranged a voltameter which could be subjected to 1500 atmospheres pressure and compared it with a similar voltameter in free air. He found no appreciable difference between them due to the pressure.

A paper by Lowry,[11] dealing with the solvent properties of silver-nitrate solutions, is an important contribution to the voltameter literature because of its bearing on the purification of silver nitrate. The paper gives quantitative data on the amount of chlorides, bromides, iodides, and sulphides held by silver-nitrate solutions at different concentrations and temperatures.

Jaeger and Von Steinwehr [12] published a short paper in 1914 referring to the names of the different types of voltameter. Prior to April, 1910, we had referred to an arrangement of the voltameter consisting of a glass dish underneath the anode as the Kohlrausch voltameter.[13] In deference to what we understood to be Dr. Jaeger's opinion on the question we ceased to call this arrangement the Kohlrausch voltameter, and subsequently referred to it as the Poggendorff voltameter. This, however, was not what was desired, and we are taking this opportunity to correct the matter. The Kohlrausch form of voltameter being especially used in Germany, it is proper to designate it according to the usage of that country. It is now our understanding that the arrangement which we have described as the Poggendorff voltameter [14] when used without silk or other organic wrapping around the anode should be called the Kohlrausch voltameter. When an organic covering of the anode is used, the instrument is not properly to be called a Kohlrausch voltameter. We show in Fig. 4 a photograph of a Kohlrausch voltameter as we have recently used it at this Bureau. The matter of names for the various types of instruments is more a matter of convenience than of vital importance. We have frequently referred to the porous-cup voltameter as the Richards voltameter, although Prof. Richards was not the first to use a porous cup around the anode.[15] In a more recent paper of Jaeger

---

[9] This Bulletin, 10, pp. 477, 486 (Reprint No. 220). [10] Zs. f. Phys. Chem., 84, p. 83; 1913. [11] Proc. R.S., 91; p. 53; 1914. [12] Elektrotech. Zs., 35, p. 819. [13] Supp. to Rept. to Internat. Com., p. 18, footnote 8. [14] This Bulletin, 9, p. 173 (Reprint No. 194). [15] The use of a porous cup is mentioned in the 1883 edition of Wiedemann's Elektricitat, p. 491. Probably Poggendorff may be said to have first used the porous cup. Pogg. Ann., 75, p. 337; 1848.

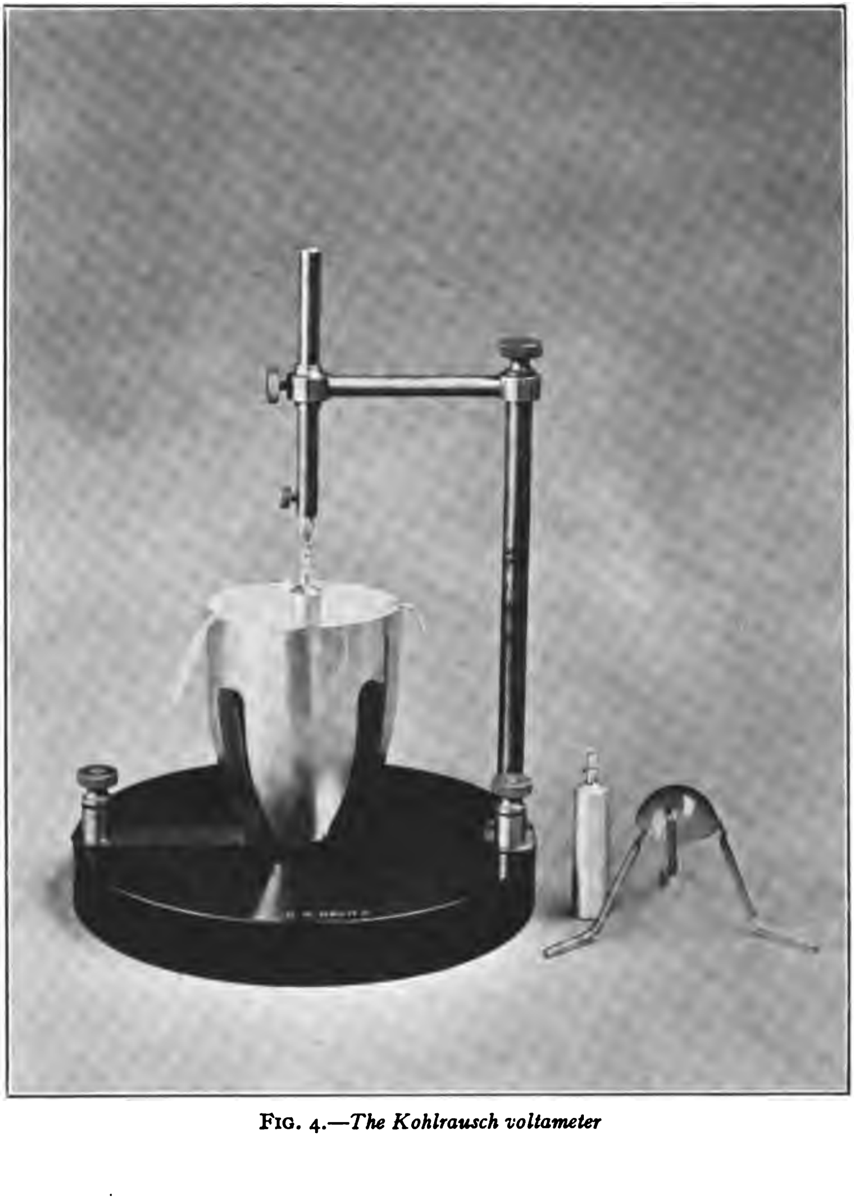


FIG. 4.—*The Kohlrausch voltameter*

and Von Steinwehr[16] they express the opinion that Richards and Anderegg have not proved their conclusions as to the inclusions in the silver-voltameter deposits, and they also state that we have not shown the volume effect in any other form of voltameter than the porous-cup form. In answer to this latter statement we have recently published[17] a rather full account of our experiments on the volume effect, including some experiments made recently.

In a note in the October (1916) number of the Journal of the American Chemical Society, Richards and Anderegg correct some statements made in their earlier paper[17a] and admit the correctness of the silver voltameter work of the Bureau of Standards, and also admit the presence of errors in their own work which vitiated their conclusions as to the magnitude of the inclusions in the silver deposit.

Since this paper has gone to press we have received a copy of Obata's paper on the voltameter.[17b] He has made careful measurements of the voltage of the Weston cell, finding 1.01826_9 volts at 20° C. He also investigated the effect of acid in the voltameter and obtained a relation almost identical with that which we gave.[17c]

III. SUMMARY OF THE VOLTAMETER WORK AT THE BUREAU OF STANDARDS[18]

When the international technical committee met in Washington in the spring of 1910 to carry out voltameter measurements and to determine the voltage of the Weston normal cell, we presented to the delegates a report[19] of our work previous to that time. This report was in the form of short paragraphs summarizing our conclusions. We have made use of much of the material in that report in what follows, but it has been rearranged and revised. In addition to this we have added the conclusions drawn from our subsequent work. To each paragraph is appended a series of references to the principal places in our papers, as published in the Bulletin, where the experimental results or a more complete discussion may be found. These references are designated by the volume and page of the Bulletin. They furnish a ready guide to the preceding papers, but can not be regarded as a complete index.

1. [20] The use of filter paper in the silver voltameter gives an abnormal deposit which is usually striated and from 1 to 5 parts in

---

[16] Zs. f. Instrk., 35, p. 225; 1915. [17] This Bulletin, 13, p. 447. [17a] J. Am. Chem. Soc., 37, p. 7. [17b] Proc. Tokyo Math. Phys. Soc., 8, p. 437, 1916. [17c] This Bulletin, 10, p. 482. [18] With the cooperation of A. S. McDaniel, S. J. Bates, G. A. Hulett, and W. M. Bovard. [19] Supp. to Rept. to Internat. Com., p. 7. [20] This Bulletin, 9, pp. 196, 199, 215, 222, 511.

10 000 too heavy. Using a minimum quantity of filter paper the effect is proportionally decreased, but an excess in weight is always found which in precise work is far too much to neglect. Different grades of filter paper produce approximately the same effect if used in equal quantities. A preliminary washing of the filter paper with dilute alkali and water reduces the excess but does not eliminate it.

2. [21] The striations and excess in weight are also produced if instead of placing the filter paper in the voltameter while the silver is being deposited it is allowed to stand in the electrolyte for a time before the latter is electrolyzed, the clear solution being poured or filtered off and electrolyzed in a voltameter without filter paper. If the electrolyte is merely filtered through filter paper before electrolysis, an appreciable increase in the weight of silver will be found. Again, if the electrolyte is made up from pure silver nitrate and distilled water in which latter filter paper has stood for some time, the deposit will be striated and too heavy. The water poured off from the filter paper contains something (oxycellulose and cellulosehydrates) extracted from the filter paper, and we have called this soluble extract for convenience "filter-paper extract."

3. [22] This effect of filter paper in producing striated deposits offered a valuable means of tracing out the nature of its action upon the electrolyte. By this means, and also other methods, the influence of filter paper upon the electrolyte was established.

4. [23] The constituents of the filter paper which are active in the voltameter are soluble in water, since aqueous extracts of filter paper produce even more pronounced effects than the filter paper itself. Yet these active substances can not be foreign impurities associated with the cellulose of the filter paper, since repeated extraction does not diminish the activity of the filter paper in the voltameter.

5. [24] Concentrated filter-paper extracts reduce neutral or faintly acid silver-nitrate solution to a wine-red colloidal solution of metallic silver under ordinary conditions. This colloidal solution is permanent in the presence of silver nitrate and other electrolytes, owing to the protective action of the reversible organic colloid which is extracted from the filter paper. This colloidal silver may be coagulated by means of alcohol. The properties and composition of this coagulated silver or hydrogel show it to be

---

[21] This Bulletin, **9**, pp. 201, 205, 213, 231, 237.

[22] This Bulletin, **9**, pp. 211, 236, 247, 251, 259, 270.

[23] This Bulletin, **9**, p. 230.

[24] This Bulletin, **9**, pp. 237, 242.

nearly pure metallic silver containing a little organic material. It changes spontaneously into ordinary gray metallic silver under certain conditions, is insoluble in ammonium-hydroxide solution, soluble in 30 per cent nitric acid, soluble in potassium cyanide, and completely amalgamates with mercury at ordinary temperatures.

6. [25] The reduction of neutral silver-nitrate solution—that is, containing no "uncombined" acid—by filter-paper extract is accompanied by the liberation of nitric acid. The detection of this "free" nitric acid is complicated, however, by the fact that silver nitrate is slightly hydrolyzed in solution and also reacts with litmus and certain other indicators. These difficulties were overcome, however, by precipitating the silver as chloride by means of pure neutral sodium or potassium chloride and filtering by means of asbestos or finely divided platinum; the test is then made upon the filtrate. Tests made in this way show that silver nitrate solution contaminated with filter-paper extract is at first basic (to the same extent as the extract itself when diluted to the same amount), but becomes less basic on standing, and finally acid.

7. [26] The action of the filter paper (cellulose) is not due to the formation of either silver nitrite or of silver hyponitrite, as suggested by Smith and Lowry, but certain other reduction products of nitric acid, notably hydrazine nitrate, when added to the electrolyte, cause the deposit to become striated. Careful tests showed, however, that none of these reduction products of nitric acid are formed in the voltameter under ordinary conditions.

8. [27] The action of salts of hydrazine, hydroxylamine, etc., in the voltameter was found to be due simply to their strongly reducing character. Any strong reducing agent capable of precipitating colloidal metallic silver from neutral silver-nitrate solution, when added to the electrolyte, causes the silver deposit to become striated similar to the deposits formed when filter paper is present. Weaker reducing agents, such as cane sugar, starch, hydrocarbons, etc., do not produce these effects. It would thus appear that cellulose (pure filter paper) is a stronger reducing agent than either cane sugar or starch, and that it is this property which causes it to produce such marked effects in the voltameter.

---

[25] This Bulletin, **9**, pp. 247, 526.

[26] This Bulletin, **9**, pp. 230, 233, 234, 235.

[27] This Bulletin, **9**, pp. 229, 235, 236, 251.

9. [28] The strong reducing action of cellulose is due to the formation of a film of oxycellulose on the surface of the fibers when exposed to the air under ordinary conditions. This very small amount of oxycellulose may be almost completely extracted with water (more completely with dilute alkali), but begins to form again immediately on exposure to the same conditions. The concentrated filter-paper extracts, especially the extracts made with dilute alkali, are straw yellow in color and yield appreciable amounts of furfuraldehyde when distilled. Dilute nitric acid increases the amount of furfural obtained by distillation. The strong reducing action of oxycellulose is not due to its decomposition into reducing sugars such as dextrose, but probably to its decomposition into furfuraldehyde. Its colloidal nature also probably influences its reducing properties.

10. [29] The oxycellulose extracted is colloidal in character, as revealed by examination with the ultramicroscope. It shows a basic reaction toward methyl orange and iodeosine, and may be accurately titrated against N/1000 acid by means of the latter indicator. It is a reversible colloid in the sense defined by Zsigsmondy. Under usual conditions it migrates toward the anode. Only a relatively small amount of this organic colloid reaches the cathode in the silver voltameter, the main portion of the excess weight of deposit in the filter-paper voltameter consisting, we believe, of colloidal metallic silver.

11. [30] Raw silk used as a septum instead of filter paper gives at first an effect somewhat similar to that of filter paper, due to its decomposition into an aldehyde; if used repeatedly, acid is produced, and this acts in the opposite direction, decreasing the weight. Sometimes, therefore, the effect of silk may be to increase the weight of the deposit, and sometimes to decrease the weight of the deposit, according to how long it has been used. Raw silk may contain linen or mercerized cotton, in which case its effect is greater. Pure raw silk thoroughly washed produces the effect only slightly.

12.[31] Polymerized furfuraldehyde when added to the electrolyte in amounts as small as 0.001 per cent causes the electrodeposited silver to become striated and strikingly similar in appearance under the microscope to the deposits from the filter-paper voltameter.

---

[28] This Bulletin, **9**, pp. 231, 232, 237, 252, 254, 256, 260.

[29] This Bulletin, **9**, p. 239.

[30] This Bulletin, **9**, pp. 201, 202, 232; **10**, p. 508.

[31] This Bulletin, **9**, pp. 236, 259.

13.[32] The most important classes of impurities to be guarded against are: (*a*) Reducing impurities both organic and inorganic; (*b*) "uncombined" base or acid; (*c*) abnormal amounts of carbon dioxide; (*d*) "soluble" or colloidal silica; and (*e*) positively charged colloids in general.

14.[33] The two fundamental conditions for striations are (1) the presence of reducing impurities in the electrolyte and (2) a motion of the electrolyte over the cathode. These must exist simultaneously, as neither can produce striations alone, although the first may modify the crystalline structure of the deposit. The distinctness and color of the striations depend on the relative amount of reducing impurities, except that in the case of a high-current density or long-continued current the striations may be bridged over by the deposited metal forming a solid sheet that does not appear striated at the end of the experiment. The deposit from a pure electrolyte, uncontaminated by filter paper or other material, is distinctly crystalline and entirely free from striations. Striations are therefore an evidence of an impure electrolyte, although slight impurity (sufficient to increase the weight appreciably, especially in a large voltameter) may exist without evident striation. The cause of striations and the conditions which determine their distance apart and appearance are fully discussed in the second paper.

15.[34] Colloidal silver in solutions prepared chemically or by Bredig's method travels to the cathode. This is a matter of importance in the explanation of striations.

16.[35] The anodes are generally prepared by slowly depositing silver upon them at the same time that the silver is removed from the platinum cups by electrolysis. This may be conveniently done during the night, using a smaller current than in the voltameter deposit. The anodes are subsequently baked, which whitens them and frees them from acid. We have also employed pure commercial silver for anodes and have found it satisfactory, but the anode slime is produced in much greater quantity than upon the electrolytic anodes, hence the latter are to be preferred, especially when no septum is used. We recommend an anode current density not greater than 0.05 ampere per square centimeter.

---

[32] This Bulletin, **9**, pp. 222–262, 524; **10**, pp. 494–495; **11**, p. 556; **13**, p. 167; **13**, p. 447.

[33] This Bulletin, **9**, pp. 200, 211, 270, 279.

[34] This Bulletin, **9**, p. 219.

[35] This Bulletin, **9**, pp. 183, 518; **10**, pp. 499, 529.

17.[36] Platinum cups of several sizes and gold cups of the smaller size have been used as cathodes. With pure electrolyte the deposits in the various sizes are in agreement. The gold cups agree with the platinum cups and are satisfactory in service, but we do not recommend them in preference to platinum because they are not as durable. The cathodes both with and without deposits have been dried at 150° in an electric oven. We have seen comparatively little floating silver when washing a deposit in any form of voltameter. This may be left in the bowl by using a siphon to remove the electrolyte and wash waters. After thorough washing with cold distilled water no spots should appear on the deposit after drying in the oven. We recommend a current density not greater than 0.01 ampere per square centimeter.

18.[37] For the accurate weighing of the cathode bowls it is necessary to have the balances in a room of nearly constant temperature and to protect the bowls from any considerable radiations. To minimize the errors arising from changes of humidity and atmospheric density we prefer to use platinum bowls of equal size as tares. With proper arrangements a 4-g. deposit is quite sufficient for weighings to be made to a higher accuracy than 1 part in 100 000 of the deposited silver.

19.[38] In washing the deposits of silver we have found it necessary to complete the washings on the same day that the experiment is made. We find that the precaution taken by some observers of soaking the deposits overnight leads to a serious error, since silver in contact with platinum is appreciably soluble in water.

20.[39] A large variety of voltameters has been used. Among them are the porous-cup form; the nonseptum form, including that designed by Kohlrausch and the modification devised by F. E. Smith, of the National Physical Laboratory; the siphon form in several different arrangements; and the filter-paper form. The last we have found is seriously in error, due to the action of filter paper. (See above.) The siphon form presents great experimental difficulties, due to its high internal resistance and the large volume of electrolyte which may lead to error. There remain, therefore, the porous-cup voltameter, which we have found particularly useful, and the nonseptum forms of Kohlrausch

---

[36] This Bulletin, **9**, pp. 170, 184, 187, 212, 221, 522; **11**, pp. 555, 567; **13**, p. 151.

[37] This Bulletin, **9**, pp. 171, 174, 181, 188; **13**, p. 152.

[38] This Bulletin, **9**, p. 184; **11**, p. 558.

[39] This Bulletin, **9**, pp. 172, 518; **10**, pp. 479, 497, 529; **13**, p. 151.

(no silk) and of Mr. Smith. These are the most reliable, in our opinion, and are in substantial agreement. But it must be noted that a voltameter without any septum may give an abnormally heavy deposit, due to anode slime carried over to the cathode, especially if the anode is very small. Some form of septum is desirable, unless a voltameter arrangement is employed which effectively prevents the formation of anode slime, or in some other way prevents anode slime from reaching the cathode.

21.[40] The $AgNO_3$ salt must be purified by recrystallization, with or without subsequent fusion, repeatedly if necessary. The preparation of the salt and the testing for purity we have fully discussed. An electrolyte prepared by dissolving pure salt in pure water does not require filtering. The deposit is, however, unaltered by filtering the electrolyte through asbestos. The presence of a trace of acid (1 or 2 parts in 1 000 000) in the electrolyte affects only slightly the weight of silver deposited. The electrolyte may become slightly acid to this extent during the run when a porous cup is used, but this does no harm.

22.[41] The water used to prepare the electrolyte has been twice distilled, its specific conductivity lying between 0.8×10^{-6} and 2×10^{-6}. In addition, special care has been taken that the water was neutral toward iodeosine (in ether-water solution) or methyl red as it came from the still.

23.[42] The restriction in the official specifications of the London conference that only 30 per cent of the silver in the electrolyte be deposited is unnecessary. Ten per cent solution of $AgNO_3$ agrees with 15 per cent in the weight of the deposit produced. Using 10 per cent solution is more economical of material, and on the whole to be preferred, provided the volume of the cathode electrolyte is not too small. Used cathode solution (made up to 10 per cent by adding pure new salt) agrees with 10 per cent new solution when the latter is pure. Used solution gives a smaller and more nearly normal deposit than new when the latter is not quite pure; this is due to the impurity being electrolyzed out during the first run.

24.[43] If recrystallized silver nitrate containing any amount of acid greater than 0.005 per cent is fused in an electric oven at a temperature between 230° and 300° C, and is quickly removed from the oven as soon as completely fused, the salt retains from 0.001 to 0.003 per cent of the nitric acid, and shows no evidence of decomposition as indicated by its reaction toward N/1000 permanganate, and by the fact that it gives no volume effect in the voltameter. Salt containing about this amount of nitric acid is, in our opinion, more suitable for voltameter work than when exactly neutral.

---

[40] This Bulletin, **9**, pp. 524, 537.

[41] This Bulletin, **9**, p. 536.

[42] This Bulletin, **9**, pp. 204, 496, 512; **10**, p. 494.

[43] This Bulletin, **9**, p. 544.

25.[44] If acid silver-nitrate crystals containing traces of organic impurities are fused as we have described, the product reduced N/1000 permanganate. This is a reliable and very sensitive test for small traces of organic material in general in silver nitrate, and is especially valuable for detecting traces of filter-paper contamination. Colloidal silver is oxidized quantitatively by permanganate, one equivalent of the silver requiring one equivalent of the permanganate solution. The anode electrolyte does not reduce thousandth normal permanganate solution if carefully decanted from the anode slime or if filtered through asbestos. If filtered through filter paper, it does reduce quite appreciable quantities of permanganate.

26.[45] We have found it possible to make satisfactory tests of the acidity of the electrolyte by precipitating the silver with a neutral chloride and titrating the filtrate with N/1000 H_2SO_4 or N/1000 NaOH, using either iodeosine in ether-water solution or an alcoholic solution of methyl red. The latter is somewhat simpler to use.

27.[46] A careful study of the effect of acid in the electrolyte has been made, showing that it decreases the deposit of silver if the electrolyte is pure. With impure electrolytes the effect can not always be predicted. Acid does not cause a deposition of hydrogen ions before the deposition of silver begins, as some have supposed.

28.[47] The temperature coefficient of the porous-cup voltameter is zero for a pure electrolyte. Experiments have shown that it is not more than 1 part in 1 000 000 per degree, at least between 20° and 50° C., and this is within the errors of the experiment. When the electrolyte contains reducing impurities these will be more active at the higher temperature and therefore a temperature coefficient will appear, as found by Lord Rayleigh and others, but this does not mean that the true electrochemical equivalent is subject to temperature changes.

---

[44] This Bulletin, 9, pp. 531, 534; 13, p. 169.

[45] This Bulletin, 9, p. 526; 10, p. 502; 11, p. 555.

[46] This Bulletin, 10, pp. 482, 503, 505; 11, p. 556.

[47] This Bulletin, 9, p. 520.

29.[48] Large voltameters frequently give larger deposits than small ones, such excess being due to the impurity of the electrolyte. This excess of the deposit in voltameters of larger volume is called the "volume effect." With very pure electrolyte the difference disappears, but we have seldom, if ever, been able to purchase silver nitrate pure enough to show no appreciable volume effect without further purification. The agreement of large and small voltameters in series is an excellent test for the purity of the electrolyte.

30.[49] The volume effect is not confined to any one form of voltameter, but has been found in all the forms tested. We have found the large and small sizes of voltameters in excellent agreement when the electrolyte was pure, as shown by our permanganate and acidity tests. With less pure electrolyte, such as we have prepared from "C. P." silver nitrate as purchased, a difference of from 0.2 to 0.8 mg appears, and by soaking a little filter paper in this electrolyte for about 10 minutes this difference may be increased to 1.5 or 2.0 mg. Since we have used the same cathodes, anodes, and porous cups in these tests, the conclusion is obvious that the volume effect arises from the electrolyte and not from the porous cup or other arrangement of the voltameter. With an electrolyte known to be impure we have never found the large and small voltameters in agreement and, on the other hand, with an electrolyte believed to be pure the volume effect has appeared to an appreciable extent in only two or three cases out of a great number of comparisons; these were undoubtedly due to experimental error or to accidental contamination of the electrolyte.

31.[50] If the volume of electrolyte in the porous-cup voltameter is specified, it should be the volume of the electrolyte in the cathode space. The volume of the anode liquid above 20 cc for a 4 g deposit is immaterial.

32.[51] The siphon form of voltameter with electrolyte as purchased has given, without exception, a larger deposit than the Richards or Kohlrausch forms as used by us. The siphon voltameter with porous cup over the cathode end gives a smaller deposit than without a porous cup, because the latter reduces the volume of the cathode electrolyte. A porous cup over the anode end makes little, if any, difference. However, with electrolyte of highest purity the siphon voltameter probably agrees with other forms, although due to heating it can not be used in absolute determinations and for large sizes it magnifies any slight volume effect.

---

[48] This Bulletin, 9, pp. 168, 514; 10, p. 530; 13, p. 167; 13, p. 447.

[49] This Bulletin, 9, p. 514; 10, p. 530; 13, p. 167; 13, p. 447.

[50] This Bulletin, 9, p. 516.

[51] This Bulletin, 9, pp. 509, 516; 10, p. 492.

33.[52] No advantage is found in using large porous-cup voltameters instead of small ones, but on the contrary several disadvantages. They require more electrolyte, can not be weighed as accurately relatively to the amount of silver deposited (unless the deposit is more than usual and more than necessary), are less convenient to handle, and are more expensive. If the salt is not perfectly pure, the excess of the deposit will be greater in the large cups and hence the error multiplied. Four grams can readily be deposited in our smallest cups, representing one-half ampere for two hours. We advise the use of more than one size of platinum cup, however, for testing the purity of the electrolyte, employing the smaller size for standard use. On the contrary, the new form devised by F. E. Smith is more convenient in the large sizes.

34.[53] The porous cups should be fine grained, thin walled, and of low electrical resistance, and after preliminary washing should be kept immersed in good $AgNO_3$ solution before using in the voltameter and between experiments. We find it easy to keep the cups neutral and clean and believe them thoroughly reliable in use. That porous cups are very efficient separators between anode and cathode chambers is shown by the fact that filter paper may be placed inside the porous cups without altering the appearance or weight of the deposit on the cathode. Filtration through a porous cup decolorizes a solution of colloidal metal and also removes the filter-paper extract from an electrolyte or from a water solution. We do not advise cleaning the porous cups with *aqua regia* and KCN nor baking them at high temperatures. We use nitric acid for whitening them and distilled water for washing. Heating to a high temperature renders them alkaline. Cups made by the Königlich Porzellan Manufaktur, of Berlin, have been used in most or our experiments, but in the later work we have also used cups made by John Maddock, in Trenton, N. J., with equal success. These latter have the advantage of being provided with solid vitreous tops. Not every kind of a porous cup will be satisfactory in the voltameter. We have tried several other kinds and have found them unsuitable, for various reasons.

---

[52] This Bulletin, **9**, pp. 503, 505.

[53] This Bulletin, **9**, pp. 185, 220, 519; **10**, p. 510; **11**, pp. 556, 569; **13**, p. 170.

35.[54] Tests on the purity of the deposits have been made in various ways. In the first place, it is to be remarked that the consistency of the results shows either that the inclusions must be very small or very constant in amount. By alloying the deposit of silver with 50 times its weight of mercury we were able to release the inclusions so as to make *actually visible* organic matter deposited in the silver from solutions which had been strongly contaminated by filter paper, and by means of phenolsulphonic acid small amounts of silver nitrate were detected; but when deposits from pure electrolytes were similarly alloyed, no visible inclusions were found nor was any evidence of silver nitrate as great as 0.001 per cent found.

An extensive and careful series of tests for inclusions has been made by heating the deposits in the platinum cups to a temperature of 600° or above, both in an electric furnace and in a flame. Consistent results were obtained, showing as the average of 25 observations a mean loss in weight of the deposit of 0.0040 per cent, which is independent of the size of the voltameter. With deposits from less pure electrolytes we have found inclusions to be greater. We have measured the inclusions between the silver crystals and the cup by an application of the conductivity method and find them to be only about 0.0002 per cent of the silver deposit as a maximum. We have found the method of heating the cups and deposits to expel the inclusions to be subject to a serious source of error, due to the slight alloying of the platinum and silver which results in platinum black when the silver is removed. This must be guarded against the next time the cups are used.

36.[55] Various experiments on the anode solution have been made, since this has been thought to contain an anomalous substance which deposits silver spontaneously and makes the deposit on the cathode too heavy if it is permitted to reach the cathode. We have found that all the effects ascribed to it may be more readily attributed to the presence of impurities in the electrolyte, such as colloidal silver. We have not found anything abnormal about anode solutions which were initially pure.

---

[54] This Bulletin, 9, p. 241; 10, p. 516; 13, p. 147.

[55] This Bulletin, 9, pp. 203, 513; 10, p. 524; 13, pp. 169, 513 (errata, line 5).

The following determinations have been made in the foregoing papers:

37.[56] The voltage of the Weston normal cell at 20° C has been found to be 1.01827 volts. For this determination three long series of observations involving about 300 deposits in the voltameters of various sizes and of both the porous-cup and nonseptum forms have been made. We have used the international ohm as it was defined by the international technical committee. The value for the cell is in international volts and is not corrected for any inclusions in the silver.

38.[57] By means of an absolute current balance of the Rayleigh type and our voltameters, using both the porous-cup and nonseptum forms, the absolute electrochemical equivalent of silver is 1.11805 mg per coulomb (not corrected for inclusions in the silver). By applying the corrections for inclusions in the silver (see No. 39 below) we find the absolute electrochemical equivalent of silver to be 1.11800 mg per coulomb.

39.[58] Measurements of the inclusions of foreign material in the silver deposits have shown that on the average 0.004 per cent of the weight of the deposit is expelled by heating. This indicates that the deposited silver from pure solution is 99.996 per cent pure silver.

40.[59] By using the silver and iodine voltameters in series and comparing the deposits of silver and iodine, the ratio of silver deposit to the iodine deposit is found to be 0.85017, which corrected for the inclusions of foreign matter in the silver deposits is 0.85013_6. This is larger than the ratio of the present international atomic weights of silver and iodine by nearly 0.018 per cent.

41.[60] In terms of the silver voltameter for calculating the coulombs on the basis of the electrochemical equivalent of silver (1.11800 mg), as defined by the London Electrical Congress of 1908, we found the electrochemical equivalent of iodine to be 1.31502 mg per coulomb. This is, then, the value in international electrical units. To convert it into the absolute value, assuming the inclusions in the silver deposits to be 0.004 per cent, as stated above, we have to add 0.004 per cent; that is, the value becomes 1.31507 mg per coulomb.

---

[56] This Bulletin, **9**, pp. 198, 504; **10**, pp. 486, 489, 490, 498.

[57] This Bulletin, **10**, p. 477.

[58] This Bulletin, **13**, p. 147.

[59] This Bulletin, **10**, p. 442.

[60] This Bulletin, **10**. p. 442.

42.[61] The Faraday on the basis of the absolute electrochemical equivalent of silver and of iodine and their atomic weights is as follows:

On the silver basis (Ag=107.88)	96 494
On the iodine basis (I=126.92)	96 512
Mean	96 503

The best round value which can be assigned to this constant appears, therefore, to be 96 500 coulombs.

43.[62] Silver deposits in platinum dishes are appreciably soluble in distilled water. The average rate at which the silver is lost from the deposit is 0.006 mg per hour from a 4 g deposit.

IV. SPECIFICATIONS FOR THE SILVER VOLTAMETER

1. PREVIOUS SPECIFICATIONS

In 1891 the electrical standards committee appointed by the English Board of Trade reported[63] at the Cardiff meeting of the British association a series of resolutions of which No. 10 defined the ampere in terms of the mass of silver deposited according to accompanying detailed specifications. At Edinburgh[64] the following year representatives of Germany, France, and the United States met with the electrical standards committee to consider the establishment of identical standards in various countries. Those present agreed "That the number 0.001118 should be adopted as the number of grams of silver deposited per second from a neutral solution of silver nitrate by a current of 1 ampere." The specifications of the preceding year were not changed, but were published again in the report of the Nottingham meeting[65] (1893), which included all the points agreed on by the international gathering at Edinburgh.

The International Electrical Congress[66] at Chicago in 1893 adopted in its chamber of delegates a resolution defining the international ampere as one-tenth of the cgs ampere and said that it was represented "sufficiently well for practical use by the unvarying current which * * * deposits silver at the rate of 0.001118 of a gram per second." This definition was accompanied by specifications which were exactly the same as in the report of the electrical standards committee, but lacked the description of the "method of making a measurement." These are therefore the first international specifications for the voltameter, but their adoption was not obligatory on the countries represented. The countries participating were invited to adopt the recommendations of the congress.

---

[61] This Bulletin, 10, p. 442.

[62] This Bulletin, 11, p. 566.

[63] B. A., Report for 1891, p. 154.

[64] B. A., Report for 1892, p. 135.

[65] B. A., Report for 1893, p. 127.

[66] Report of congress, pp. 17, 20, 1893; Coast and Geodetic Survey Bulletin 30.

The United States, by an act[67] approved July 12, 1894, was the first to adopt the recommendations of the Chicago congress, although the wording of the act was slightly modified from that of the resolutions adopted by the congress, and the duty of preparing specifications for the use of the voltameter was laid on the National Academy of Sciences. The specifications which they adopted were essentially those of the congress with the "method of making a measurement" of the English electrical standards committee added, but both were slightly modified in wording.

A few weeks later a British order in council,[68] August 23, 1894, adopted the recommendations of the Chicago congress with specifications including the method of making a measurement as previously reported by the electrical standards committee.

A decree[69] of the President of France April 25, 1896, adopted the voltameter for the practical measurement of the ampere with specifications similar to those of the electrical standards committee of the British Board of Trade.

In Germany the law[70] of June 1, 1898, adopted the voltameter and empowered the Bundesrath to fix the conditions under which the silver is to be deposited. The German law differed in some important respects from the resolutions of the Chicago congress. Some other countries also adopted similar laws for the electrical units. The next important step was taken at the Leicester[71] meeting of the British association, where more elaborate specifications were reported as a proposal from the National Physical Laboratory for discussion at the electrical congress at London the following year.

The London congress[72] made a distinction between the ampere and the international ampere. The latter they defined in terms of the silver voltameter, but the meager specifications adopted represented only the principal points on which there was no difference of opinion, and it was the intention that the international committee should adopt more detailed and rigorous specifications, but this has not yet been done.

---

[67] Coast and Geodetic Survey Bulletin No. 31; Standards for Electrical Measure, Nat. Acad. Sci., 1895.

[68] B. A., Report for 1894, p. 136.

[69] This Bulletin, 1, p. 75, 1904; Circular No. 60, p. 62, 1916.

[70] This Bulletin, 1, p. 72, 1904; Circular No. 60, p. 60, 1916.

[71] B. A., Report for 1907, p. 76.

[72] Report of London congress, p. 72; 1908.

The specifications adopted by the London congress are as follows:

SPECIFICATION RELATING TO THE DEPOSITION OF SILVER

The electrolyte shall consist of a solution of from 15 to 20 parts by weight of silver nitrate in 100 parts of distilled water. The solution must only be used once, and only for so long that not more than 30 per cent of the silver in the solution is deposited.

The anode shall be of silver, and the kathode of platinum. The current density at the anode shall not exceed $\frac{1}{5}$ ampere per square centimetre and at the kathode $\frac{1}{50}$ ampere per square centimetre.

Not less than 100 cubic centimetres of electrolyte shall be used in a voltameter.

Care must be taken that no particles which may become mechanically detached from the anode shall reach the kathode.

Before weighing, any traces of solution adhering to the kathode must be removed, and the kathode dried.

Dr. Rosa, at the request of the members of the international technical committee, prepared a new set of voltameter specifications, but these were not adopted although published[73] by the technical committee in its report.

Although the specifications for the voltameter are not yet adopted, Switzerland by Federal law[74] of June 24, 1909, and England by order in council of January 10, 1910, adopted the recommendations of the London conference, and legislation[75] on this subject had passed the Chamber of Deputies of France prior to the outbreak of the European war. The specifications which we publish below are the outcome of our own work on the voltameter and we hope they will be of service when it is possible for the international committee to adopt specifications.

2. SPECIFICATIONS PROPOSED BY THE BUREAU OF STANDARDS

These specifications, which are the outcome of the Bureau's experiments of the past eight years, are prepared for work of the highest precision and must be closely followed when an accuracy of 0.001 per cent is desired. To attain this degree of precision, the utmost care as to the purity of the materials and in the manipulation of the voltameters is necessary, and the result should be the mean of several separate experiments with two or more voltameters in series in each experiment.

For work requiring only 0.01 per cent accuracy, the precautions taken may be somewhat reduced. The labor of weighing the deposits and purifying the salt may be considerably lessened as compared with the procedure for work of the highest accuracy, provided the unpurified electrolyte does not contain more than 25 parts in 1 000 000 of acid, or enough alkali to produce striation. No observations should be used in which the deposits show striations. The mean of several deposits should be taken.

---

[73] Report of Int. Tech. Com., p. 199; 1912. [74] Circular No. 60, p. 63; 1916. [75] Circular No. 60, p. 57; 1916.

For work requiring only 0.1 per cent accuracy, the c. p. silver nitrate, prepared by the best manufacturing chemists, may be used without further purification. Filter paper in minimum amounts may be used as a septum between anode and cathode, for convenience, if desired. The deposits will then be striated, but deposits showing excessive striations of a leaden color should not be relied on. With careful manipulation, the mean of two deposits should give results of the desired accuracy.

THE SPECIFICATIONS.*

1. The electrolyte shall consist of a solution of silver nitrate in distilled water (1), having from 10 to 20 g (2) of silver nitrate in 100 cc of the solution.

2. The electrolyte must be free from organic or other reducing substances and colloids, as shown (*a*) by a suitable chemical test (3), (*b*) by giving a crystalline deposit free from striations (4), and (*c*) by giving the same weight of a deposit in a large and in a small voltameter (5).

3. The silver nitrate may be purified by crystallization from acid solution and fusion, and if the chemical test for purity is omitted, it should be purified until further crystallization from acid solution and subsequent fusion does not change the weight of the deposit (6).

4. The voltameter should contain not less than 75 cc in the cathode chamber (7), and the deposit should not continue long enough to reduce the concentration of the electrolyte at the surface of the cathode chamber below 5 per cent (8).

5. The electrolyte when ready for use must be neutral or slightly acid, as tested by methyl red or iodeosin (9). As 1 part in 1 000 000 of base may increase (10) the deposit appreciably, it may be better to have a slight acidity (say 1 part in 1 000 000) than to take the risk of making it slightly basic in attempting to make it strictly neutral. The electrolyte must be neutral at the end of the experiment, or, if not, only a trace of acid or base should be present. Any septum or other substance which contaminates the electrolyte, or makes it basic, or produces more than a trace of acid must be avoided (11).

---

* Numbers in parentheses refer to supplementary notes following the specifications.

6. The cathode is most conveniently a crucible or bowl, preferably of platinum (although gold (12) may be used), of from 125 to 400 cc capacity (13). The surface should preferably be smooth and bright, and the deposited silver should be removed each time by electrolysis (14) or by acid without scratching or marring the surface of the platinum by any instrument.

7. The anode should be of pure silver and is preferably (15) coated with electrolytic silver (16). The anode should have as large an active area as the size and type of voltameter permit (17).

8. The current during a deposit should be maintained constant, and is preferably not more than 1 ampere, and the time not less than one hour (18).

9. If the surface of the platinum is perfectly clean and the electrolyte pure, the silver will be adherent and there will be little, if any, loose silver (19). After thorough washing (20), the cathode bowls are dried at about 150° C, preferably in an electric oven, and after cooling are weighed (21). In the weighing a similar platinum dish, adjusted to the same weight, is advantageously used as a tare.

10. The electromotive force of the standard cell employed is calculated from the weight of silver deposited (22), the resistance (23), and the time (24), using 1.11800 mg per coulomb (25) as the electrochemical equivalent of silver (26).

11. If a septum between the anode and cathode is used (27), it must not contaminate the electrolyte with organic or reducing impurities (28); it must not produce acid or alkali in the electrolyte (29); and it must be of sufficiently fine grain to hold back the anode slime without introducing any high resistance into the voltameter (30).

3. SUPPLEMENTARY NOTES

1. The water should be of the best quality and free from CO_2. It should not be more than 1×10^{-6} alkaline or acid, and its conductivity should not be more than 2×10^{-6} reciprocal ohms (resistance 500 000 ohms per cubic centimeter). The water and electrolyte should be kept in bottles of insoluble glass. A bottle long used for the purpose is much better than a new one. The electrolyte should not be stored in glass vessels for long periods, but fused solid $AgNO_3$ may be preserved indefinitely.

2. The lower limit of concentration is safe and economical for cathode current densities up to 0.01 ampere per square centimeter. Higher concentrations are useful for large current densities and

for small voltameters, in which convection currents can not replenish the impoverished liquid at the cathode as freely as in the large voltameters.

3. This test is for reducing impurities, and consists in adding N/1000 $KMnO_4$ solution (1 cc at a time) to 10 cc of a 66 per cent solution of the $AgNO_3$ (acidified) until the color persists for five minutes. It is described in volume 9, page 531.

4. A deposit made from pure electrolyte presents a white matte surface, and under the microscope is seen to be made up of crystals having mirror-like faces and sharp angles. When impurities which increase the mass of deposit by 2 to 5 parts in 10 000 are present, the crystals become very irregular and the deposit appears striated. For excessive amounts of impurities the crystalline structure vanishes, the striations become very prominent, and the color of the deposit is often gray or yellowish.

5. Heavier deposits are obtained in large voltameters than in small voltameters if reducing impurities are present in the electrolyte. The agreement of two different sizes is one criterion for the purity of the electrolyte, and is particularly useful if any colloids have escaped detection by the permanganate test.

6. The purest $AgNO_3$ purchased from the best manufacturing chemists may be used in some cases for work requiring 0.01 per cent accuracy (providing there is no striation and no appreciable volume effect), but, in general, this is not the case and it can not be depended upon to be sufficiently good for the most precise work. The means used to further purify it are somewhat dependent on the nature and amount of impurities that it contains. In most cases a preliminary fusion of the crystals (slightly acidified with HNO_3) serves to oxidize the organic impurities. Colloidal silver and some other impurities appear to collect at the surface and may be partially removed after the salt has solidified by washing the surface or by filtration. If the salt is now pearl white, one recrystallization from acid solution and fusion (care being taken not to overheat the salt and thereby expel the last trace of acid) will usually complete the purification. Some of the mother liquor should always be tested for turbidity by greatly diluting it with distilled water, since chlorides, sulphides, and some other substances which are, relatively speaking, soluble, in concentrated silver nitrate might otherwise escape detection. Before making up the electrolyte the surface of the fused cake should be again washed. The fusions may be made in a platinum dish, which should be

lifted out of the furnace as soon as the last trace of solid salt has melted.

7. When a porous-cup voltameter is used, the cathode chamber is that space occupied by the electrolyte outside of the porous cup. When a nonseptum voltameter (Smith's form) is used, the cathode chamber means the space outside of the glass parts when the latter are closed, as before or after an experiment.

8. The concentration in the electrolyte in contact with the cathode is much reduced during the deposit. If the electrolyte becomes too impoverished at the cathode, the fall of potential at the cathode may be increased sufficiently to liberate hydrogen, and a slimy deposit of silver is then obtained which does not accurately represent the quantity of electricity that has passed through the voltameter as computed from the electrochemical equivalent of silver and can not be accurately weighed. The electrolyte may become turbid, due to finely divided silver in suspension.

9. The iodeosin (10 mg per liter) is dissolved in ether and kept over a layer of water. Before adding 2 cc of the ether solution of the indicator to 10 cc of the $AgNO_3$ solution the Ag must be precipitated as AgCl by neutral KCl and filtered off. The acid or base that the filtrate contains is then determined by titration, using N/1000, H_2SO_4, or NaOH as required. This test is described in volume 9, page 526. The methyl-red indicator is a 0.2 per cent solution of methyl red in alcohol. One drop or two, at the most, is added to the filtrate and the titration made as described above.

10. When the base (AgOH) has been produced by overfusion of silver nitrate or by the addition of other hydroxides, it is usually in the colloidal state and will slightly increase the weight of the deposit. Acid in pure electrolyte tends to decrease the deposit slightly; 1 part of acid in 1 000 000 parts of electrolyte produces about 4½ parts in 1 000 000 difference in deposit on the average. Above 10 parts of acid in 1 000 000 the effect is proportionally slightly less.

11. Filter paper at first renders the $AgNO_3$ solution basic, owing to the basic reaction of the oxycellulose and cellulose hydrates, but later, owing to the reducing action on the $AgNO_3$, the solution becomes acid. Raw silk when first used acts similarly to filter paper, but later yields a small amount of acid, which renders the $AgNO_3$ solution slightly acid without the precipitation of silver. This is further explained in the Report of the International Technical Committee, page 174.

12. Platinum is preferable to gold because it is more durable. There appears to be no difference in weight between deposits made on gold and platinum.

13. The errors due to manipulation increase where sizes larger or smaller than these limits are used. The provisional specifications of the London conference provide that the current density at the cathode shall not exceed 1/50 ampere per square centimeter. It seems best, now, that this should be changed to 1/100 ampere per square centimeter, particularly if the concentration of electrolyte is 10 g of salt in 100 cc of solution.

14. This is most conveniently done by allowing a small current to flow through the voltameter overnight or until the silver has all been removed.

15. More anode slime is formed on bare silver anodes than on those coated with electrolytic silver. In voltameters without septum this may cause trouble if the slime escapes from the glass trap arranged to confine it.

16. This is conveniently done when a previous deposit is being removed from the cathode bowl, using a relatively small current. Before use the anode should be heated to 200° or more to expel any acid that may have come from the solution.

17. The trouble with anode slime is greatly reduced by increasing the size of the anode. The provisional specifications of the London conference provide that the current density shall not exceed 1/5 ampere per square centimeter. This is allowable, but it is better to have the current density much smaller. Electrolytic silver increases the active area of the anode considerably over what the same anode would have if bare.

18. Before starting the current through the voltameters, it is desirable to estimate as nearly as possible the resistance of the voltameters, and adjust the total resistance so that the current will start at its correct value as closely as possible. It is essential to have means of quickly adjusting the current to the precise value, and also a convenient adjustment to counterbalance the drift or fluctuations in the current during the progress of the experiment.

19. Any loose silver drawn off in the electrolyte or wash waters should be carefully saved and added to the bowl before weighing the deposit.

20. The deposits should be washed only with pure distilled water, which should be tested occasionally for $AgNO_3$ with KBr as it is drawn off. By this means 1 or 2 parts in 100 000 of the

silver salt can easily be detected. A more sensitive method, however, is to make conductivity measurements of the water after drawing it off for comparison with its initial conductivity. Several wash waters should be used after no $AgNO_3$ can be detected by KBr in the liquid drawn off. The washings, which are usually five to seven in number for each cathode, should be done without delay. It is not advisable to soak the deposits in water overnight. When washing the bare platinum bowl preparatory to an experiment, acids and alkalies may be used. After the bowl has been prepared for weighing preliminary to the deposit, it should not be touched with the bare hand until the whole experiment has been completed.

21. In making the weighings, care must be exercised to protect the bowls and balance from even very slight changes in temperature. The bowls should be in perfect equilibrium with the temperature and humidity of the balance case.

22. The weight of silver (corrected to vacuo) is expressed in milligrams.

23. The resistance of the standard across the terminals of which the drop is potential is made equal to the voltage of the cell to be measured, is expressed in international ohms.

24. The time is expressed in mean solar seconds and should be recorded on a chronograph. The timing circuit should not be electrically connected to the voltameter circuit, owing to the possibility of leakage currents affecting the mass of silver deposited.

25. This is according to the decision of the London conference.

26. $$\text{Emf} = \frac{\text{weight of deposit} \times \text{resistance}}{1.11800 \times \text{time}}$$

27. The function of a septum between the anode and cathode is to prevent the slime formed on the anode during electrolysis from reaching the cathode. A porous cup of pukal ware is useful for this purpose, when it is properly prepared. If no septum is used, a suitable and efficient glass trap to catch the slime must be provided.

28. This occurs when filter paper, silk, blotting paper, and similar substances are used.

29. These effects are also produced by the materials mentioned above (28) and by the porous cup if not properly prepared. The free alkali of the porous material should be eliminated by filtering dilute HNO_3 and water through the pores, followed by several portions of the best $AgNO_3$. The pores should be completely

filled with electrolyte before use. Between experiments the cups should be kept immersed in the best electrolyte. The porous cups become stained with use, but this does not seriously affect the results obtained with them. They may be whitened by filtering strong (not concentrated) HNO_3 through the pores, which, however, must be completely washed out with water before saturating the pores with the neutral $AgNO_3$ preparatory to use in the voltameter. Satisfactory cups for the purpose are made of pukal ware, and are about 60 mm high, 35 mm diameter, and 1 mm thick, as manufactured by the Königlich Porzellan Manufaktur in Berlin and by John Maddock, Trenton, N. J.

30. The resistance of the septum should preferably not exceed 2 ohms.

WASHINGTON, April 5, 1916.

APPENDIXES

Appendix A.—BIBLIOGRAPHY OF THE SILVER VOLTAMETER WITH A FEW PAPERS ON CLOSELY ALLIED SUBJECTS

During the progress of the Bureau's work on the silver voltameter a considerable file of references to papers bearing on the voltameter has been accumulated. From this file the following bibliography has been compiled. Although a number of previous papers on the silver voltameter have contained reviews of the literature, we have not found in any of these as complete a list as we append below. We believe that it contains all of the principal papers dealing with the silver voltameter. In addition, we have included a number of papers in which the silver voltameter was used for measuring the electric current in the course of investigations on other subjects. We have also included a few papers not dealing specifically with the silver voltameter, but on closely allied topics. Such papers are on the following subjects: Various forms in which silver is deposited, properties of silver-nitrate solutions; the formation of silver peroxynitrate; the ratio of the atomic weights of silver and iodine; the validity of Faraday's laws; the definition of the fundamental electrical units; and a few papers of historical interest dealing with the beginnings of voltametric measurements.

The papers are arranged alphabetically, according to the name of the author. We have indicated the title or subject of the paper in English, but we have not given the exact title in every case. This is because references to reports of institutions, etc., are usually to paragraphs without formal titles, or, on the contrary, some papers have titles that are excessively long, while in still other cases the title does not convey an idea of our particular interest in the paper. In general, however, we have given the exact title. The references are given with the usual abbreviations, and we think they will readily be understood without the necessity of listing the full names of the journals as a key to the abbreviations. We have not included any references to the voltameter from compendiums of physics (except one case of historical interest), encyclopedias, handbooks of engineering, or textbooks. It is rather surprising, however, to find how crude and inaccurate many of these descriptions are. In the index of the last edition of one of the largest and best-known encyclopedias it is surprising to read "Voltameter, see Voltmeter."

Bibliography

Name	Title or subject	Reference
Abegg and Pick	Influence of silver nitrate on the solubility of silver nitrite.	Ber. Deut. Chem. Gesel., 38, p. 2571; 1905.
Almeida	Decomposition of salts dissolved in water.	Ann. d. Chim. et Phys., III, 51, p. 257; 1857.
Arons	Determination of the Verdet constant	Wied. Ann., 24, p. 161; 1885.
de Baillehache	Electrical units	1909.
Do	Fixing the units by legislation	Rev. Gen. Sci., 24, p. 17; 1913.
Do	The silver voltameter	Lumiere Electr., 22, p. 44; 1913.
Do	Electrical units and French legislation.	Electr., 75, p. 56; 1915.
Bartorelli	On the behavior of a voltameter with platinum electrodes.	Phys. Zs. 4, p. 850; 1904.
Bates and Vinal	Comparison of the silver and iodine voltameters and the determination of the Faraday.	J. Am. Chem. Soc., 36, p. 916; 1914.
Baümler	Separation of energy losses in the voltameter.	Zs. f. Elektrochem., 12, p. 481; 1906.
Baxter	On the atomic weights of silver and iodine.	Carnegie Publication No. 135.
Do	A revision of the atomic weights of silver and iodine.	J. Am. Chem. Soc., 32, p. 1591; 1910.
Beach	On the copper voltameter	Am. J. Sci., 46, p. 81; 1893.
Behn	On the striated arrangement of galvanic deposits.	Wied. Ann., 51, p. 105; 1894.
Betts	Phenomena of metal depositing	Trans. Am. Electrochem. Soc., 8, p. 63.
Betts and Kern	The lead voltameter	Trans. Int. Elec. Cong., St. Louis, 2, p. 67, 1904; Electr., 54, p. 16, 1904; Metall., 1, p. 430, 1904.
Board of Trade	Reports of electrical standards committee dealing with voltameter specifications.	B. A. Reports for 1891, p. 154; for 1892, p. 135; for 1893, p. 127; for 1894, p. 136; for 1907, p. 77; Electrician, 27, p. 325, 1891. A. I. E. E. 10, p. 17, 1893.
Boerema	Electromotive force of the Weston cell in international units.	Arch. Neer. Sci., 3, p. 336; 1914.
Boltzmann	Researches on the silver voltameter	Sitzber. Akad. Sci., Wien., IIA, 121, p. 1051; 1912.
Do	Historical review of the electrical units, their definitions and the international standards.	Sep. Abdruck. Mit. des K. K. Versuch., II, pts. 3 and 4; 1913.
Bose	Validity of Faraday's law	Chem. Zeit., 26, pp. 47 and 66; 1902.
Bose and Conrat	A silver microvoltameter	Zs. f. Elektrochem., 14, p. 86; 1908.
British Assoc. Report No. 38.	Experiments on septs for the voltameter.	Portsmouth Meeting, p. 82; 1911.
Buckner and Hulett	Studies on the silver coulometer	Trans. Am. Electrochem. Soc., 22, p. 367; Int. Cong. App. Chem., 26, p. 565; 1912.
Bundesrath	Regulations issued by the Bundesrath for the use of the silver voltameter.	Zs. f. Instrk., 21, p. 180; 1901.
Bureau of Standards	Announcement of a change in the value of the international volt.	Bu. Stds. Circular No. 29; 1910.
Do	The silver voltameter	Annual Report, Director of Bu. Stds., p. 47; 1915.
Do	Electrical units and standards	Bu. Stds. Circular No. 60; 1916.
Carhart	Electromotive force of a Daniell cell	Am. J. Sci., 28, p. 374; 1884.
Do	Report of committee on standards of measurement.	Proc. A. A. A. Sci., p. 71; 1900.
Carhart, Willard, and Henderson.	A new electrolyte for the silver voltameter.	Trans. Am. Electrochem. Soc., 9, p. 375; Phys. Rev., 23, p. 189; 1906.
Cohen	Validity of Faraday's law at high pressures.	Zs. f. Phys. Chem., 84, p. 83; 1913.
Dahr	Inaccuracies in the copper voltameter	Zs. f. Elektrochem., 19, p. 746; 1913.
Danneel	On the electrolytic separation of metals.	Zs. f. Elektrochem., 4, p. 154; 1897.
Datta and Dahr	Accuracy of the copper voltameter	J. Am. Chem. Soc., 38, p. 1156, 1916.
Dede	On the copper voltameter	Zs. f. Elektrochem., 17, p. 238; 1911.
Duschak and Hulett	Studies on the silver coulometer	Trans. Am. Electrochem. Soc., 12, p. 257; 1907.
Dellinger	The international system of electric and magnetic units.	Bull. Bu. Stds., Sci. paper No. 292. (In press.)
Edlund	Researches on the heat changes at the poles of a voltameter.	Wied. Ann., 19, p. 287; 1883.
Egoroff	Preliminary work of preparing the standards of the primary electrical units.	Rep. Bureau Wts. and Meas., Petrograd, p. 122; 1911.
Electricus (pseud)	Priority claim for the invention of the voltameter.	Sturgeon's Ann. of Elec., 1, p. 505; 1836.
Eisenreich	On the use of silver-fluoride solution in the silver coulometer.	Zs. f. Phys. Chem., 76, p. 643; 1911.
von Ettingshausen	On the Clark cell	Zs. f. Elektrotech., 2, p. 484; 1884.
Faraday	First voltameter	Exper. Researches, 1, p. 217, 1834; Phil. Trans., p. 91, 1834.
Farup	On a new silver voltameter	Zs. f. Elektrochem., 8, p. 569, 1902.

Bibliography—Continued

Name	Title or subject	Reference
Fechner	Electrochemical remarkableness of silver nitrate.	Pogg. Ann., 47, p. 1, 1839.
Ferringer	Determination of the international ampere and volt by the silver voltameter and Weston cell.	Electritchestvo 35, 13, p. 260, 1914.
Feustel	On voltameters with and without silk (activities of the Reichsanstalt).	Za. f. Instrk., 30, p. 115, 1910.
Foerster	On the copper voltameter	Za. f. Elektrochem., 3, p. 493, 1896.
Gay-Lussac and Thenard.	Early experiments in electrochemical decomposition.	Recherches Physico-Chimiques, 1, p. 12, 1811.
Glazebrook	Electromotive force of standard cells	Nature, 85, p. 508, 1911.
Do	The ohm, the ampere, and the volt, 1862–1912.	J. Inst. El. Eng., 50, p. 560; Electr., 70, p. 1014; 1913.
Glazebrook and Skinner.	On the Clark cell	Phil. Trans., 183 A, p. 567; 1892.
Gore	Electrolytic balance of chemical corrosion.	Nature, 27, p. 326; 1883.
Gray	On the electrolysis of silver and copper and the standardization of electric meters.	Phil. Mag., 22, p. 389; 1886.
Griffiths	Errors in electrical units affecting the mechanical equivalent of heat.	Nature, 56, p. 259; 1897.
Guthe	Determination of electrical units by an absolute electrodynamometer.	Phys. Za., 1, p. 235; 1900.
Do	A study of the silver voltameter	Bull. Bu. of Stds., 1, p. 21, 1904; Phys. Rev., 18, p. 445; 19, p. 138, 1904.
Do	The silver voltameter	Trans. Int. El. Cong., St. Louis, 2, p. 96; Trans. Am. Electrochem. Soc., 6, p. 96; 1904.
Do	The silver coulometer	Bull. Bu. of Stds., 1, p. 349; 1905.
Do	Absolute electromotive force of standard cells.	Bull. Bu. of Stds., 2, p. 33; 1906.
Do	Electrochemical equivalent of silver	Ann. d. Phys., 20, p. 429; 1906.
Haga and Boerema	Electromotive force of Weston normal cells.	Arch. Neer. Sci., IIIa, 3, p. 324; 1914.
Henderson	Thermoelectric behavior of silver (electrochemical paper).	Phys. Rev., 23, p. 101; 1906.
Hering	Table of electrochemical equivalents and their derivatives with examples.	Electrochem. Ind., 1, p. 170; 1903.
Do	Uniformity in electrochemical equivalents.	Trans. Am. Electrochem. Soc., 3, p. 291; 1903.
Do	Remarks on effect of gas in voltameter cathodes.	Trans. Am. Electrochem. Soc., 12, p. 293; 1907.
Herroun	An iodine voltameter	Phil. Mag., 40, p. 91; 1895.
Higgins	Remarks on originality of Faraday's voltameter.	Proc. Lond. Elec. Soc., p. 135; 1837.
Hughes and Withrow	Character of silver deposits from various electrolytes.	J. Am. Chem. Soc., 32, p. 1571; 1910.
Hulett and Vinal	Studies on the silver voltameter	Bull. Bu. of Stds., 11, p. 553, 1914; J. Wash. Acad. Sci., 4, p. 593, 1914; J. Phys. Chem., 19, p. 173, 1915.
International Conference on Electrical Units.	Report	Charlottenburg, 1905 (Gedruckt in dem Reichsdruckerei 1906).
International Electrical Congress.	.....do	Chicago, 1893.
Do	.....do	London, 1908.
International Technical Committee.	.....do	Washington, 1910; report published 1912.
Jaeger	Electrical standards	Trans. Int. Cong., St. Louis, 1, p. 331; 1904.
Jaeger and Lindeck	Silver voltameter (activities of the Reichsanstalt).	Za. f. Instrk., 26, pp. 122 and 157; 1906.
Jaeger and von Steinwehr.	Investigation of the silver voltameter	Za. f. Instrk., 28, pp. 327, 353; 1908.
Do	Silver voltameter (activities of the Reichsanstalt).	Za. f. Instrk., 29, p. 114; 1909.
Do	Remarks on the silver voltameter	Elektrotech. Za., 35, p. 819; 1914.
Do	On the inclusion of electrolyte in the silver deposits and the volume effect.	Za. f. Instrk., 35, p. 225; 1915.
Jaeger, Lindeck, and von Steinwehr.	The silver voltameter (activities of the Reichsanstalt).	Za. f. Instrk., 28, p. 112; 1908.
Janet	Electrical units	Bull. Int. Soc. Electr., 3, p. 950; 1913.
Janet, Laporte, and de la Gorce.	Electrochemical equivalent of silver	Bull. Int. Soc. Electr., 8, p. 523; Trav. Lab. Centr. d'Elec., 2, p. 288, 1908.
Kahle	On the Clark cell	Za. f. Instrk., 12, p. 117; B. A. Report for 1892, p. 148; Elektrotech. Za., 13, p. 407, 1892.
Do	Silver voltameter (activities of the Reichsanstalt).	Za. f. Instrk., 16, p. 215, 1896; 17, p. 145, 1897; 19, p. 212, 1899.

Bibliography—Continued

Name	Title or subject	Reference
Kahle	Silver voltameter	Zs. f. Instrk., 18, pp. 229 and 267, 1898; Wied. Ann., 67, p. 1, 1899.
Kahlenberg	Electrodeposition of metals from nonaqueous solvents.	J. Phys. Chem., 4, p. 349; 1900.
Kirmis	On the forms of electrolytically deposited silver.	Pogg. Ann., 158, p. 121; 1876.
Kistiakowsky	Silver titration voltameter	Zs. Elektrochem., 12, p. 713; 1906.
Koepsel	Constant of electromagnetic rotation of polarized light.	Wied. Ann., 26, p. 476; 1885.
Do	Determination of the electrochemical equivalent of silver.	Wied. Ann., 31. p. 268; 1887.
Kohlrausch	On the electrochemical equivalent of silver.	Pogg. Ann., 149, p. 170; 1873.
Do	On determinations of F. and W. Kohlrausch with reference to the anode liquid.	Ann. d. Phys., 26, p. 580; 1908.
Kohlrausch, F. and W	Preliminary communication of results on electrochemical equivalent of silver.	Sitzber d. Phys.-Med. Gesel., Würtzburg, p. 41; 1884.
Do	On the electrochemical equivalent of silver.	Wied. Ann., 27, p. 1; 1886.
Kohlrausch and Weber	Electrochemical equivalent and temperature.	Ann. d. Phys., 26, p. 409; Deut. Phys. Gesel., 9, p. 681, 1907.
Kohlschutter and Schacht.	Forms of deposited metal—III. Influence of foreign substances.	Zs. f. Elektrochem., 19, p. 172; 1913.
Kohlschutter and Toropoff.	Forms of deposited metal—I. Black silver.	Zs. f. Elektrochem, 19, p. 161; 1913.
Köthner and Aeuer	On the atomic weight of iodine	Lieb. Ann. d. Chem., 337, pp. 123, 362; 1904.
Kreider	Iodine titration voltameter	Am. J. Sci., 20, p. 1; 1905.
Laird and Hulett	Inclusions in electrolytic silver and their effect on the electrochemical equivalent.	Trans. Am. Electrochem. Soc. 22, p. 345; Int. Cong. App. Chem., 26, p. 599, 1912.
Do	Electrochemical equivalent of cadmium	Trans. Am. Electrochem. Soc., 22, p. 385; 1912.
Laporte and de la Gorce	On the electrochemical equivalent of silver.	Trav. Lab. Cent. d'Elec., 2, p. 318; Bull. Int. Soc. Electr., 10, p. 157; C. R., 150, p. 278, 1910.
Leduc	On the electrolysis of silver nitrate	Electrochemie, 3, p. 151.
Do	Electrochemical equivalent of silver, copper, and water.	Rapp. Cong. Int. de Phys., Paris, 2, p. 440; 1900.
Do	Electrolysis of silver nitrate	J. d. Phys., 1, p. 561, 1902; C. R., 135, p. 23, 1902.
Do	On the electrochemical equivalent of silver.	C. R., 135, p. 237; Electrochem., 8, p. 127, 1902; Electricien, 24, p. 132, 1902.
Do	Electrolysis of a mixture of salts	C. R., 135, p. 395; 1902.
Lewis	Silver-bromide voltameter	J. Am. Chem. Soc., 31, p. 1145; 1909.
Lowry	The silver voltameter—Part III. The solvent properties of silver nitrate.	Proc. R. S., 91, p. 53; 1914.
McDaniel	Chemistry of the silver voltameter	Science, 34, pp. 32, 159; 1911.
Mascart	On the absolute measurement of current by electrolysis.	C. R., 93, p. 50; 1881.
Do	On the electrochemical equivalent of water.	J. d. Phys., 1, p. 109; 1882.
Do	On the electrochemical equivalent of silver.	J. d. Phys., 3, p. 283; 1884.
Mather and Smith	A comparison of the Board of Trade ampere balance with that at the N. P. L.	Proc. R. S., 80, p. 383; 1908.
Mathers and German	Mercurous perchlorate voltameter	Ind. Univ. Stud., p. 41; 1910.
Mendenhall	Legal units of electric measure	Science, 1, p. 9, 1895; Coast and Geodetic Survey Bulletins Nos. 30 and 31; Coast and Geodetic Survey Report for 1893, part 2, appendix 7, p. 173.
Merrill	Influence of temperature, pressure, etc., on deposits of silver voltameters.	Phys. Rev., 10, p. 167; 1900.
Minet	Study of the voltameter as a standard	Lumiere Electr., 22, p. 49; 1886.
Miscellaneous Notes and Discussions.	Referring particularly to Van Dijk's work.	Electr., 52, p. 613; 1903.
Do	On Faraday's law	Electrochem. Ind., 1, p. 153; 1903.
Do	On the lead and silver voltameters	Electr., 54, p. 43; 1904.
Do	Importance of the electrochemical equivalent and various determinations of it.	Electrochem. Ind., 2, p. 116; 1904.
Do	Review of the voltameter situation	Electrochem. Ind., 2, p. 288; 1904.
Do	The silver voltameter	Electr. World, 60, p. 1243, 1912; 63, p. 350, 1914.
Do	Final results with the silver voltameter.	Electr. Rev., 62, p. 890; 1913.
Do	On the silver voltameter	Electr. Rev., 62, p. 886; 1913.
Do	Silver and iodine voltameters	Electr. World, 64, p. 454; 1914.
Mulder	Silver peroxynitrate	Rec. Trav. Chim., 17, p. 129; 1898.
Mulder and Heringa	do	Rec. Trav. Chim., 15, p. 1; 1896.

Bibliography—Continued

Name	Title or subject	Reference
Myers	On the influence of dissolved gases on the silver voltameter.	Wied. Ann. 55, p. 288; 1895.
Mylius	The silver voltameter (Activities of the Reichsanstalt).	Za. f. Instrk., 22, p. 155; 1902.
Mylius and Dietz	On the purity of silver for anodes (Activities of the Reichsanstalt).	Za. f. Instrk., 21, p. 151; 1902.
National Academy of Science.	Standards for electrical measure	Judd and Detweiler, Washington; 1895.
Naumann and Rucker	Influence of silver nitrate on the solubility of silver nitrite.	Ber. Deut. Chem. Gesel., 38, p. 2292; 1905.
Novak	Studies on the silver voltameter	Proc. Roy. Boh. Acad. Sci., Prague, 1, p. 387; 1892.
Obata	The silver voltameter	Proc. Tokyo Math. Phys. Soc., II, 8, p. 437, 1916.
Patterson and Guthe	A new determination of the electrochemical equivalent of silver.	Phys. Rev., 7, p. 257; Proc. A. A. A. Sci., 47, p. 155; 1898.
Pécheux	Determination of certain atomic weights by voltameter methods.	C. R., 154, p. 1419; 1912.
Perot and Fabry	Measurement of Clark cells in international volts.	Ann. de Fac. Sci., Marseille, 8, p. 201; 1898.
Pellat and Leduc	Determination of the electrochemical equivalent of silver.	C. R., 136, p. 1649; 1903.
Poggendorff	First silver voltameter	Pogg. Ann., 70, p. 181; 1847.
Do	First use of a porous cup in a silver voltameter.	Pogg. Ann., 75, p. 337; 1848.
Do	An early illustration of Poggendorff's voltameter.	Wied. Galv., 1st ed., 1, p. 314; 1861.
Potier	On the electrochemical measure of the intensity of electric currents.	C. R., 108, p. 396; 1889.
Potier and Pellat	Electrochemical equivalent of silver	J. d. Phys., 9, p. 381; 1890.
Rayleigh	On the absolute measurement of current.	Proc. Camb. Phil. Soc., V, p. 50; 1883.
Do	On the accuracy of voltameter measurements.	Nature, 56, p. 292; 1897.
Rayleigh and Sedgwick	On the electrochemical equivalent of silver.	Proc. R. S., 36, p. 448; 37, p. 142; 1884.
Do	do	Phil. Trans., 175 A, p. 411; 1884.
Richards	Note concerning the silver coulometer	Proc. Am. Acad. Sci., 44, p. 91; 1908.
Richards and Anderegg	Inclusions in the silver voltameter deposits.	J. Am. Chem. Soc., 37, p. 7; 1915; Chem. News, 112, pp. 172, 181, 1915.
Do	Complications at the anode of the silver voltameter.	J. Am. Chem. Soc., 37, p. 675; 1915.
Do	Note on Inclusions	J. Am. Chem. Soc., Oct., 1916.
Richards, Collins, and Heimrod.	Electrochemical equivalents of copper and silver.	Proc. Am. Acad. Sci., 35, p. 123, 1899; Za. f. Phys. Chem., 32, p 321; 1900.
Richards and Forbes	Quantitative synthesis of silver nitrate.	J. Am. Chem. Soc., 29, p. 808; 1907.
Richards and Heimrod	On the accuracy of the improved voltameter.	Proc. Am. Acad. Sci., 37, p. 415; Za. f. Phys. Chem., 41, p. 302; 1902.
Richards and Stull	Validity of Faraday's law	Za. f. Phys. Chem., 42, p. 621; 1902.
Riesenfeld	Gas voltameters with nickel electrodes	Za. f. Elektrochem., 12, p. 621; 1906.
Rodger and Watson	Magnetic rotation of polarized light	Phil. Trans., 186A, p. 630; 1895.
Rosa	The silver voltameter as an international electrical standard.	Science, 34, p. 32; 1911.
Rosa, Dorsey, and Miller.	International ampere in absolute measure.	Bull. Bu. of Stds., 8, p. 367.
Rosa and Vinal	The silver voltameter, Part I	Bull. Bu. of Stds., 9, p. 151; J. Wash. Acad. Sci., 2, p. 451; Elec. World, 60, p. 1261, 1912; Elektrotech. Za., 34, p. 232, 1913.
Do	The volume effect in the silver voltameter.	Bull. Bu. of Stds., 13, p. 447; 1916.
Rosa, Vinal, and McDaniel.	Effect of filter paper on the mass and form of deposit in silver voltameter.	Phys. Rev., 30, p. 658; 1910.
Do	The silver voltameter, Part II	Bull. Bu. of Stds., 9, p. 209; J. Wash. Acad. Sci., 2, p. 509; Elec. World, 60, p. 1262, 1912; Elektrotech. Za., 34, p. 233, 1913.
Do	The silver voltameter, Part III	Bull. Bu. of Stds., 9, p. 493; J. Wash. Acad. Sci., 3, p. 40; Elec. World, 60, p. 84, 1913; Elektrotech. Za., 34, p. 1168, 1913.
Do	The silver voltameter, Part IV	Bull. Bu. of Stds., 10, p. 475; J. Wash. Acad. Sci., 4, p. 52; Elec. World, 63, p. 373, 1914; Elektrotech. Za., 35, p. 789, 1914.
Rosa and Wolff	Work of the international technical committee.	J. Wash. Acad. Sci., 2, p. 259; 1912.
Schuster and Crossley	Electrolysis of silver nitrate in vacuo	Proc. R. S., 50, p. 344; 1892.
Shaw	Verification of Faraday's law with reference to silver and copper.	B. A. Report for 1886, p. 318.
Do	On the atomic weights of silver and copper.	Phil. Mag., 23, p. 138; 1887.

Bibliography—Continued

Name	Title or subject	Reference
Shrimpton	On the atomic weight of copper	Proc. Lond. Phys. Soc., 26, p. 292; 1914.
Skinner	Comparison of voltameters containing different solvents.	B. A. Report for 1901, Appendix to No. 28 report on El. Stds., p. 601.
Smith	Experiments with the silver voltameter.	Report of Nat. Phys. Lab. for 1906, p. 27.
Do	Practical standards for electrical measurements.	Electr., 61, pp. 844 and 876; Elec. Eng., 4, p. 389; 1908.
Do	The silver voltameter	Rev. Gen. Sci., 19, p. 171; 1908.
Do	A comparison of salt from different sources in the silver voltameter.	Report of Nat. Phys. Lab. for 1909, p. 33.
Do	Description of new form of voltameter.	Report of Nat. Phys. Lab. for 1910, p. 32.
Do	On electrostenolysis in the silver voltameter.	Report of Nat. Phys. Lab. for 1911, p. 33.
Do	Review of Bureau of Standards work.	Rev. Gen. Sci., 24, p. 216; 1913.
Do	Present condition of work on electrical units at National Physical Laboratory.	British Assoc. Report for 1907, p. 75.
Smith, editor	British Association reports on electrical standards.	Cambridge University press, 1913.
Smith, Mather, and Lowry.	The silver voltameter	Phil. Trans., 207A, p. 545, Col. Researches, Nat. Phys. Lab. 4, p. 125, 1908. Report of Nat. Phys. Lab. for 1907, p. 30.
Snowdon	Electrolytic precipitation of silver	J. Phys. Chem., 9, p. 392; 1905.
von Steinwehr	Silver voltameter measurements	Zs. f. Instrk., 33, pp. 321 and 353; 1913.
von Steinwehr and Feustel.	The silver voltameter (activities of the Reichsanstalt).	Zs. f. Instrk., 31, p. 122; 1911.
Stephan	Determination of electrochemical equivalent of metals without weighing.	Zs. f. Phys. und Chem. Unter., Berlin, 23, pp. 150 and 288; 1910.
Sturgeon	Criticism of Faraday's voltameter	Sturgeon's Ann. of Elec., 1, p. 369; 1836.
Sulc	Silver peroxynitrate	Zs. f. Anorg. Chem., 24, p. 305; 1900.
Tanatar	So-called silver peroxynitrate	Zs. f. Anorg. Chem., 28, p. 331; 1901.
Thompson, S. P.	Remarks on electrical standards and the work of the inter. technical committee.	J. Inst. Elec. Eng., 50, p. 310; 1912.
Thöldte	Galvanic polarization	Ann. d. Phys., 18, p. 1061; 1906.
Tommassi	On the electrolysis of silver nitrate	Electrochimie, 8, p. 161; 1902.
Van Dijk	Electrochemical equivalent of silver	Arch. Néer. Sci., 9, p. 442, 1904; Handl. Ned. Gen. Cong., 10, p. 135; 1905.
Do	Influence of heating the silver voltameter to redness on the electrochemical equivalent.	Arch. Neer. Sci., 10, p. 277; 1905.
Do	The silver voltameter	Gebroeders Hoitsema, Groningen; 1905.
Do	The electrochemical equivalent of silver.	Ann. d. Phys., 19, p. 249 and 21, p. 845; 1906.
Van Dijk and Kunst	A determination of the electrochemical equivalent of silver.	Ken. Akad. Weten., Amsterdam, 6, p. 441, 1903; Versl. Wis. Nat. K. K. Akad. Wet., 12, p. 637, 1903; Ann. d. Phys., 14, p. 569, 1904.
Vanni	On the apparent variations in the electrochemical equivalent of copper.	Wied. Ann., 44, p. 214, 1891; Lum. Electr., 42, p. 192, 1891; Electr., 28, p. 12, 1891.
Vinal	Experiments with different types of voltameters.	Sci., 34, p. 31; 1911.
Vinal and Bates	Comparison of the silver and iodine voltameters and the value of the Faraday.	Bull. Bur. of Stds., 10, p. 425; J. Wash. Acad. Sci., 4, p. 69, 1914.
Vinal and Bovard	Inclusions in the silver voltameter deposits.	Bull. Bur. of Stds., 13, p. 147; J. Am. Chem. Soc., 38, p. 496, 1916.
Vogel	On the state in which silver comes down by reduction in the wet process.	Pogg. Ann., 193, p. 316; 1862.
Washburn and Bates	The iodine coulometer and the value of the Faraday.	J. Am. Chem. Soc., 34, pp. 1341 and 1515; 1912.
Watson	Value of the earth's field in international units.	Phil. Trans., 198A, p. 431; 1902.
Do	Silver dioxide and peroxynitrate	J. Chem. Soc., 89, p. 578; 1906.
Weber	Determination of the electrochemical equivalent of silver.	Unknown, see Lumiere Electr., 22, p. 51; 1886.
Weston	Remarks on organic matter and silver oxide in the voltameter.	Trans. A. I. E. E., 6, p. 330; 1889.
Whitney	A silver titration voltameter	Zs. f. Elektrochem., 12, p. 713; 1906.
Wilcox	Validity of Faraday's law at low temperatures.	J. Phys. Chem., 13, p. 384; 1909.
Wohwill	Crumbling of the anode	Zs. f. Elektrochem., 9, p. 311; 1903.
Wolff	The so-called international units	Bull. Bur. of Stds., 1, p. 39, 1904; Trans. Int. El. Cong., St. Louis, 1, p. 148, 1904.
Do	Principles involved in the selection of the fundamental electrical units.	Bull. Bur. of Stds., 5, p. 243; 1908.

Appendix B.—ERRATA TO OUR PRECEDING PAPERS

Some few errors in our previous papers have come to our attention. None of these are serious so far as the reading of the papers is concerned except the two errors in designating the curves in Figs. 1 and 3 of the paper entitled "Studies on the silver voltameter" as published in the Journal of Physical Chemistry. In these two cases the manuscript as it left the authors' hands was correct. The changes that caused these errors were made without the knowledge of the authors.

Except for these corrections and a few mistakes in the footnotes it would be unnecessary to publish these errata so far as the other corrections are concerned:

Errata.

Subject	Publication	Change
1. The Silver Voltameter, Part I.	This Bulletin, 9, p. 153..	Footnote 6, instead of volume "140" read "149."
Do................	This Bulletin, 9, pp. 154–155.	Footnotes 13, 14, 15, instead of "Ann. d. Phys." read "Wied. Ann."
Do................	This Bulletin, 9, p. 156..	Footnote 22, instead of page "631" read "630."
Do................	This Bulletin, 9, p. 157..	Footnote 29, instead of volume "8" read "7, p. 257."
Do................	This Bulletin, 9, p. 158..	Line 19, the data for this experiment were accidentally omitted from the second paper. It is as follows: Feb. 12, 1910. Two cups containing silver deposits were filled with electrolyte and allowed to stand two hours, when they were washed and dried as usual. Newly prepared electrolyte which had been contaminated with filter paper was put in cup No. 125 and the deposit in this cup appeared to gain 0.09 mg. The electrolyte put in cup No. 126 was clear anode liquid taken from inside of several porous cups after an ordinary experiment. The deposit in this cup appeared to lose 0.03 mg.
Do................	This Bulletin, 9, p. 160..	Line 27, instead of "Snowden" read "Snowdon."
Do................	This Bulletin, 9, p. 161..	Footnotes 45 and 46, instead of "El. ch." read "Electrochem."
Do................	This Bulletin, 9, p. 173..	Middle of the page, instead of "Poggendorff" read "Kohlrausch." For the explanation of this change, see page 484 of this paper. We shall not attempt to indicate in this errata the many places which this change involves.
Do................	This Bulletin, 9, p. 202..	Footnote 68, after "Phil. Trans. A186" insert "p. 630."
Do................	This Bulletin, 9, p. 204..	Footnote 70, instead of "second paper" read "third paper, page 512."
Do................	J. Wash. Acad. Sci., 2, p. 453.	Line 26, instead of "former" read "latter."
Do................	J. Wash. Acad. Sci., 2, p. 455.	Line 10, instead of "they" read "the cathodes."
Do................	J. Wash. Acad. Sci., 2, p. 456.	Line 3 from end, instead of "1.018287" read "1.01828_7."
2. The Silver Voltameter, Part II.	This Bulletin, 9, p. 223..	Footnote 9, instead of "Elec. ch." read "Electrochem."
Do................	J. Wash. Acad. Sci., 2, p. 511.	Line 11, instead of "1000" read "300."
Do................	Elect. World, 60, p. 1262.	Line 3 from end of page, instead of "1000" read "300."
Do................	Electrotech., Zs., 34, p. 233.	Middle of last column, instead of "1000" read "300."
3. The Silver Voltameter, Part III.	This Bulletin, 9, p. 498..	Line 3 from bottom, instead of "Frankfort" read "Frankfurt."
Do................	This Bulletin, 9, p. 502..	Sixth column of table, take out "second half."
Do................	This Bulletin, 9, p. 515..	Footnote 6, insert "10, p. 157."
Do................	This Bulletin, 9, p. 523..	Footnote 7, instead of "Elec. chem" read "Electrochem."
4. The Silver Voltameter, Part IV.	This Bulletin, 10, p. 488..	Footnote 13 applies to the first line of Nov. 15 and not to Nov. 5.
Do................	This Bulletin, 10, p. 489..	Second observation of Feb. 20, "large size" ought to be in "medium size."
Do................	This Bulletin, 10, p. 490..	Footnote 15 applies also to the observations of Mar. 12.
Do................	This Bulletin, 10, p. 510..	Line 14 of text, add the following: "Dr. von Steinwehr has explained to us since this was written that he does not consider this form of voltameter with silk as a Kohlrausch voltameter."

Errata—Continued

Subject	Publication	Change
4. The Silver Voltameter, Part IV.	This Bulletin, 10, p. 518	Footnote 34, instead of page "246" read "262."
Do	This Bulletin, 10, p. 524	Footnote 41, instead of page "64" read "1364."
Do	This Bulletin, 10, p. 536	Conclusion 4 has led to misunderstanding on the part of those who have apparently not read the more detailed discussions which precede it. It should be expanded to read as follows: "We have made some experiments on the inclusions of the deposited silver and conclude that when pure electrolyte is used the inclusions are very small or very constant in amount, so that the voltameter as a standard instrument for the measurement of electric current is satisfactory when used according to proper specifications."
Do	J. Wash. Acad. Sci., 4, p. 56.	Line 29, instead of "0.053 mg" read "0.53 mg."
5. Comparison of the Silver and Iodine Voltameters, etc.	This Bulletin, 10, p. 437	Footnote 7, add "and p. 494, reprint No. 201."
Do	do	Line 3 from bottom, omit one of the three l's in "especially."
Do	This Bulletin, 10, p. 443.	Line 23, instead of "Amer" read "Aeuer."
Do	do	Footnote 15, instead of "Ann. d. Phys." read "Lieb. Ann. d. Chem."
6. Studies on the Silver Voltameter.	This Bulletin, 11, p. 557	Line 15, instead of "Table 10" read "Table 11" (this error in first printing only).
Do	This Bulletin, 11, p. 558	Line 7, instead of "was" read "were."
Do	This Bulletin, 11, p. 566	Table 9 should be Table 10 (this error in first printing only).
Do	This Bulletin, 11, p. 568	Table 10 should be Table 11 (this error in first printing only).
Do	This Bulletin, 11, p. 569	Table 11 should be Table 12 (this error in first printing only).
Do	J. Wash. Acad. Sci., 4, p. 594.	Line 14, instead of "to it stand" read "it to stand."
Do	J. Phys. Chem., 19, p. 179.	Line 7, instead of "Table X" read "Table XI."
Do	J. Phys. Chem., 19, p. 183.	Fig. 1, the curve marked "I" should be "II", and vice versa to correspond with the text on pages 182 and 186.
Do	J. Phys. Chem., 19, p. 187.	Fig. 3, the curve marked "I" should be "II" and vice versa to correspond with the text on page 187.
Do	J. Phys. Chem:, 19, p. 188.	"Table IX" should be "Table X."
Do	J. Phys. Chem., 19, p. 190.	"Table X" should be "Table XI."
Do	J. Phys. Chem., 19, p. 191.	"Table XI" should be "Table XII."
7. Inclusions in the Voltameter Deposits.	J. Am. Chem. Soc., 38, p. 498.	Table I, in compiling this table one observation was overlooked, but this omission has no significant effect on the mean result or the conclusions drawn from it. This table as published in the Bulletin of the Bureau of Standards is complete.

DETERMINATION OF ALUMINIUM AS OXIDE

By William Blum

CONTENTS

Page
I. Introduction........ 515
II. General principles........ 516
III. Historical........ 516
IV. Precipitation of aluminium hydroxide........ 518
  1. Hydrogen electrode studies........ 518
    (a) The method........ 518
    (b) Apparatus and solutions employed........ 518
    (c) Results of hydrogen electrode experiments........ 519
    (d) Conclusions from hydrogen electrode experiments........ 520
  2. Selection of an indicator for defining the conditions of precipitation........ 522
  3. Factors affecting the form of the precipitate........ 524
  4. Precipitation in the presence of iron........ 525
V. Washing the precipitate........ 525
VI. Separation from other elements........ 526
VII. Ignition and weighing of the precipitate........ 528
  1. Hygroscopicity of aluminium oxide........ 529
  2. Temperature and time of ignition........ 529
  3. Effect of ammonium chloride upon the ignition........ 531
VIII. Procedure recommended........ 532
IX. Confirmatory experiments........ 532
X. Conclusions........ 534

I. INTRODUCTION

Although a considerable number of precipitants have been proposed for the determination of aluminium, direct precipitation of aluminium hydroxide by means of ammonium hydroxide, followed by ignition to oxide, is most commonly used, especially if no separation from iron is desired, in which latter case special methods must be employed. While the general principles involved in this determination are extremely simple, it has long been recognized that certain precautions in the precipitation, washing, and ignition are necessary if accurate results are to be obtained. While, however, most of these details have been studied and discussed by numerous authors, it is noteworthy that few publications or textbooks have taken account of all the factors. In the present paper it seems desirable, therefore, to assemble the various recommendations and to consider their basis and their accuracy. No attempt has been made, however, to include a complete bibliography.

II. GENERAL PRINCIPLES

In precipitations of metallic hydroxides by means of ammonia or other bases the process may be considered as a progressive hydrolysis, brought about by the neutralization of the acid continuously set free. In the case of such hydroxides as ferric hydroxide, which are practically insoluble in bases, it may be readily shown that the solubility is decreased and precipitation rendered more complete by the addition of an excess of the precipitant, thereby increasing the hydroxyl ion concentration. However, in the case of amphoteric hydroxides, such as aluminium hydroxide, it is obvious that an excess of the base is to be avoided, and it therefore becomes desirable to select that degree of alkalinity which will insure most nearly complete precipitation and at the same time avoid resolution of the precipitate. As will be shown later, the study of the progress of the precipitation and the selection of the proper "end point" of precipitation can readily be accomplished by means of the hydrogen electrode, the conditions selected being subsequently defined by means of suitable indicators.

III. HISTORICAL

Early recognition of the fact that when considerable excess of ammonia is used in the precipitation of aluminium hydroxide appreciable amounts of aluminium pass into the filtrate, led to the time-honored procedure of boiling out most of the free ammonia. The latter method, however, has its defects, owing to the attack of glass vessels by the hot ammoniacal solution (leading to contamination of the precipitate with lime, silica, etc.); and to the possible re-solution of alumina, when through excessive boiling the solution becomes slightly acid. Various authors have therefore urged the use of a very slight excess of ammonia with only a short period of boiling,[1] especially when a considerable amount of ammonium chloride is present in the solution.[2] While the beneficial effect of ammonium chloride in reducing the solubility of aluminium hydroxide in ammonia has been pointed out by numerous authors and has formed a basis for the procedures recommended in most textbooks, few attempts have been made to explain this effect, which in some cases has been attributed to the coagulation of the colloidal aluminium hydroxide by the salt.[3] While undoubtedly this is an important function of the ammonium chloride, it will be shown later that the reduction of the alkalinity (hydroxyl ion concentration) of ammonia by the presence of ammonium chloride also exerts a marked influence upon the amount of aluminium hydroxide held in solution.

---

[1] S. L. Penfield and D. N. Harper, Amer. J. Sci., **32**, p. 107, 1886; Chem. News, **54**, pp. 90, 102, 1886; W. H. Daudt, J. Ind. Eng. Chem., **7**, p. 847, 1915.

[2] Malaguti and Durocher, Ann. Chim. Phys. (3), **17**, p. 421, 1846; J. Hanamann, Z. anal. Chem., **3**, p. 367, 1864; C. F. Cross, Chem. News, **39**, p. 161, 1879; L. Blum, Z. anal. Chem., **27**, p. 19, 1888; G. Lunge, Z. angew. Chem., p. 634, 1889.

Recognition of the errors attendant upon precipitation of aluminium with ammonia has led to the recommendation of other precipitants by means of which the maximum alkalinity of the solution is restricted; for example, ammonium sulphide, ammonium carbonate, sodium bicarbonate, ammonium nitrite, phenylhydrazine, and a mixture of potassium iodide and iodate. While for special cases—for example, the separation of aluminium from iron—one or more of the above methods may have special advantages, it may be shown that for general purposes their use is in no way preferable to that of ammonia under proper conditions, and that in most cases they present practical disadvantages.

While numerous authors recommend the customary method of using an indicator such as litmus paper to detect roughly the presence of an excess of ammonia, few, if any, have suggested the accurate definition of the desired alkalinity by means of suitable indicators. Hinrichsen used rosolic acid in a study of the effect of fluorine[4] upon the precipitation of aluminium hydroxide by ammonia, but gives no experimental or theoretical basis for its selection. Numerous authors, in efforts to develop methods for the volumetric determination of aluminium, or for testing the neutrality of aluminium salts, have used various indicators for determining the beginning and completion of the precipitation of aluminium hydroxide; but few, if any, have shown that complete precipitation actually occurs at the color change selected.

---

[3] A. Classen, Quantitative Analysis, p. 145, sixth Ger. edition; 1912.

[4] Zts. anorg. Chem. 58: p. 88; 1908. In this paper Hinrichsen showed that fluorine may hinder or entirely prevent the precipitation of aluminium hydroxide by ammonia.

IV. PRECIPITATION OF ALUMINIUM HYDROXIDE

1. HYDROGEN ELECTRODE STUDIES

(*a*) THE METHOD.—The application of the hydrogen electrode to a study of the changes taking place in solution during precipitations was suggested in a paper on the determination of magnesia in limestone,[5] and was elaborated in an article by J. H. Hildebrand,[6] in which are given numerous curves for such precipitations, including the action of sodium hydoxide upon aluminium sulphate. The principle of the method is very simple, involving the measurement of the electromotive force of a cell consisting of a calomel half cell and a hydrogen electrode immersed in the solution to be investigated. The hydrogen ion concentration of the solution may then be calculated from the formula

$$\log \frac{1}{[H^+]} = \frac{\pi - 0.338}{0.058}$$

where π is the observed emf in volts at 25° C.

(*b*) APPARATUS AND SOLUTIONS EMPLOYED.—The apparatus and method of measurement were essentially those used by Hildebrand and Harned. The solution to be titrated was maintained at about 25° in a beaker which was closed with a rubber stopper having suitable perforations for (*a*) the hydrogen electrode, (*b*) the connection with a cell containing saturated potassium-chloride solution (used to eliminate the contact potential), which cell was in turn connected with a calomel half cell in 0.1 *N* potassium-chloride solution, (*c*) the tip of the burette, and (*d*) an exit tube for the hydrogen. By this arrangement carbon dioxide was conveniently expelled from the original solution by means of a current of hydrogen and was excluded during the titration. The emf readings were made at about 10-minute intervals by means of a millivoltmeter and capillary electrometer. The readings usually became constant to 1 or 2 millivolts within 20 minutes.

The aluminium-chloride solution, prepared from recrystallized aluminium chloride, was about decimolar (for $AlCl_3$) and contained a small amount of free hydrochloric acid. The sodium and potassium hydroxide solutions, prepared from the metals with exclusion of carbon dioxide, were about fifth normal. Fifth normal ammonium hydroxide was prepared by dilution of a sample of "C. P." ammonium hydroxide, furnished in a ceresin bottle, and which by evaporation (of 100 cc) was found to contain a very small amount of organic matter, but no detectable amount of nonvolatile material.

---

[5] J. H. Hildebrand and H. S. Harned, Orig. Com., Eighth Intern. Cong. Appl. Chem., 1, p. 217; 1912.

[6] Jour. Am. Chem. Soc., 35, p. 864; 1913.

(*c*) RESULTS OF HYDROGEN ELECTRODE EXPERIMENTS.—The data obtained by measurement of the changes in hydrogen ion concentration occurring upon addition of alkaline hydroxides to solutions of aluminium chloride are shown graphically in Fig. 1. The abscissas represent cubic centimeters of alkaline hydroxide

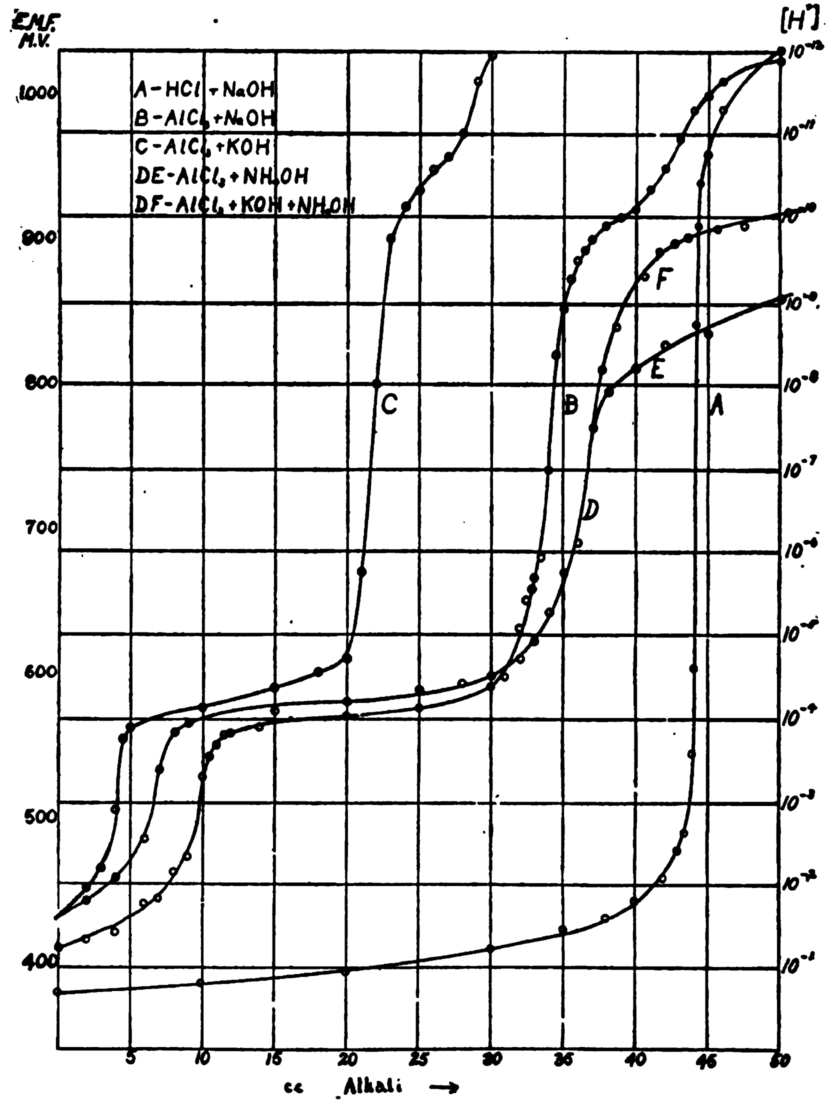


FIG. 1.—*Precipitation of aluminium hydroxide*

added, and the ordinates on the left are the observed emf values expressed in millivolts. On the right side the value of the ordinates is expressed in terms of hydrogen ion concentration, calculated as previously stated. Curves *A*, *B*, and *C* are the same as were published in a preceding article by the author[7] on the constitution of aluminates. The curve *A* for the neutralization of hydrochloric acid with sodium hydroxide is shown simply to indicate the normal course of such a reaction in the absence of any metals precipitable as hydroxides. While curves *B* and *C* are chiefly of interest in relation to the formation of aluminates, they are included here in order to show the similarity in the course of the precipitations with fixed alkalies and with ammonia.

The curve *DE* shows the progress of the reaction when ammonium hydroxide is added to a solution of aluminium chloride containing a small amount of free acid. In order to eliminate the influence of ammonium chloride (to which reference will be made later) the curve *DF* was plotted, in which the portion *F* was obtained by the addition of ammonium hydroxide to a solution, in which the aluminium hydroxide had been exactly precipitated by the addition of a calculated amount of potassium hydroxide. While the curve *F* should strictly, therefore, be attached to curve *C'*, it has been placed in its present position in order to emphasize the comparsion between the effect of ammonium hydroxide with and without the presence of ammonium chloride. The curves *E* and *F* may contain slight errors arising from small losses of ammonia during the passage of the hydrogen. Their approximate shape and position is, however, clearly indicated.

(*d*) CONCLUSIONS FROM HYDROGEN ELECTRODE EXPERIMENTS.—From the curves shown in Fig. 1 it is evident that the changes taking place during the precipitation of aluminium chloride are practically independent of the alkali used. In general, it may be seen that precipitation[8] begins when $[H^+]$ is about 10^{-3} and is complete before $[H^+]$ is 10^{-7}. In the case of the fixed alkalies it was pointed out in a former paper that appreciable re-solution of the precipitate, probably with the formation of aluminates, occurs soon after the neutral point is passed; for example, when [H$^+$] is less than 10^{-9}. When ammonium hydroxide is used as the precipitant, it may be seen from the curve *DE* that it is difficult to obtain a solution in which [H$^+$] is less than 10^{-9}, even when appreciable excess of ammonia is present. While, therefore, as is to be expected, it is not possible by this method to obtain complete solution in ammonia of any considerable quantity of aluminium hydroxide, an appreciable amount was always found dissolved[9] in any solutions in which [H$^+$] is less than 10^{-9}.

---

[7] W. Blum, J. Am. Chem. Soc., **35**, p. 1499; 1913.

[8] By "precipitation" in this sense is meant the chemical formation of $Al(OH)_3$, which (especially in the absence of salts) may not actually coagulate or form a visible precipitate until from one-third to one-half of the alkali required for complete precipitation has been added. The point at which a visible precipitate occurred in the different experiments was found to be very variable. The formation of such regular curves as are shown, however, indicates the improbability of the existence in solution of any definite basic salts such as have been supposed to be formed by solution of freshly precipitated aluminium hydroxide in neutral aluminium chloride or sulphate solutions. Consult H. W. Fischer, Habilitationsschrift, Breslau, 1908, Chem. Zentr., I, p. 260, 1909; R. Kremann and K. Hüttinger, Jahr. K. K. Geol. Reichsan, **58**, p. 637, 1909 Chem. Zentr., II, p. 1200, 1909.

The effect of even small amounts of ammonium chloride in reducing the alkalinity of ammonium hydroxide is clearly shown by comparison of the curves *E* and *F*, there being present no ammonium chloride in *F*, and in *E* only the amount equivalent to about 37 cc of 0.2 *N* NH_4OH; that is, the solution at the end was about 0.08 *N* in NH_4Cl. This effect of ammonium chloride is also illustrated in Fig. 2, in which the hydrogen ion concentration of various ammonia-ammonium chloride solutions has been calculated from the ionization constant of ammonia at 25°[10]

$$\frac{[NH_4^+]\,[OH^-]}{[NH_4OH]} = 1.8 \times 10^{-5}$$

and that of water $K_w = 1.1 \times 10^{-14}$

upon the assumption that the mass law holds for such solutions. For the sake of simplicity the ionization of ammonium chloride, which in solutions from *N* to 0.1 *N* varies from 75 to 85 per cent[11] has been taken as 80 per cent. For convenience the results have been expressed in cc of *N* ammonium hydroxide present in a volume of 100 cc of ammonium-chloride solutions of various concentration.

---

[9] *Existence of Ammonium Aluminate.*—In a previous communication the evidence in favor of the formation in solution of definite aluminates of sodium and potassium was presented. While no such definite evidence of the existence of ammonium aluminate is available, owing to the above-mentioned impossibility of securing ammonia solutions of high alkalinity, there seems to be no reason to doubt the analogy of the solutions in ammonia and the fixed alkalies. In this connection it is interesting to consider the evidence presented by C. Renz (Ber., **36**, III, p. 2751; 1903). This author dismisses the possibility of the existence of an ammonium aluminate, even though by an indirect method, viz, solution of $Al(OH)_3$ in $Ba(OH)_2$ and subsequent addition of $(NH_4)_2SO_4$, he was able to obtain a clear solution free from Ba^{++} and $SO_4^{=}$, 50 cc of which contained 0.1 g Al_2O_3. The fact, observed by Renz, that freshly precipitated $Al(OH)_3$ is readily soluble in organic amines, far from being an argument against the existence in solution, of ammonium aluminate, would appear to indicate that by the solution of aluminium hydroxide in any base aluminates are formed, the maximum concentration being dependent upon the alkalinity of the resultant solution and its consequent ability to repress the hydrolysis of the aluminate.

[10] A. A. Noyes and R. B. Sosman, Electrical conductivity of aqueous solutions, Carn. Inst. Pub., **63**, p. 228; 1908.

[11] F. W. G. Kohlrausch and L. Holborn, Leitvermögen der Elektrolyte, p. 159; 1898.

From Fig. 2 it is evident that (1) even small additions of ammonium chloride cause a marked decrease in the alkalinity of ammonium hydroxide solutions; (2) above 0.5 N an increase in the concentration of ammonium chloride has little effect; and (3) with any reasonable concentration of ammonium chloride, it is impracticable to so limit the alkalinity that a solution in which $[H^+]$ is less than 10^{-8} (that is, one which dissolves appreciable $Al(OH)_3$) is not formed when any large excess (for example, 5 cc) of concentrated ammonia is added. (It should be noted that 50 cc N NH_4OH about equals 3.3 cc conc. NH_4OH, sp. gr. 0.90.)

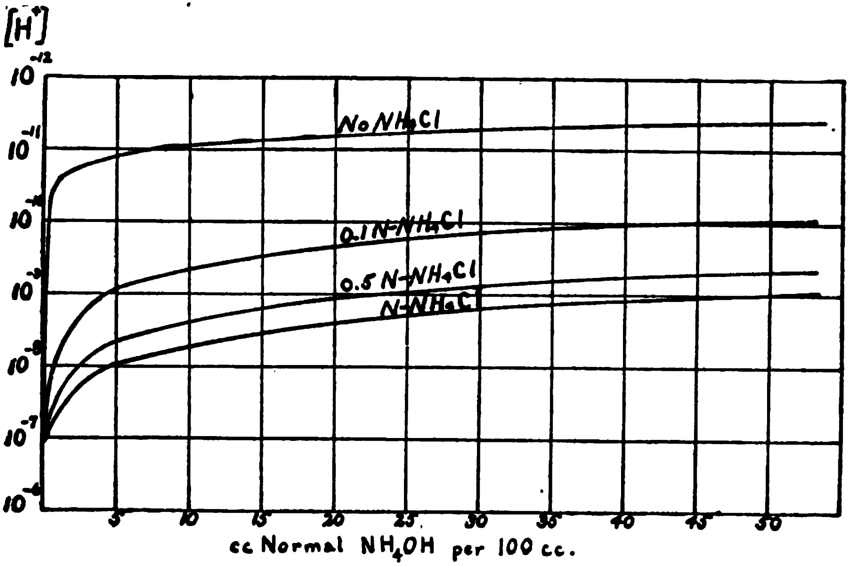


FIG. 2.—*Effect of ammonium chloride upon the alkalinity of ammonium hydroxide*

2. SELECTION OF AN INDICATOR FOR DEFINING THE CONDITIONS OF PRECIPITATION

If, as previously shown, precipitation of aluminum hydroxide by ammonia is complete before $[H^+]$ is 10^{-7}, and its re-solution is appreciable when $[H^+]$ is 10^{-8}, it is desirable to obtain some indicator which will change color when $[H^+]$ is about 10^{-7}. Experiments were therefore conducted with a few common indicators showing marked color changes near this point, viz, para-nitrophenol, methyl red, rosolic acid, and phenolphthalein. Litmus was not included because of its gradual color change. In each case the solution of the aluminium chloride and indicator contained in a platinum dish was heated just to boiling, and pure ammonium hydroxide (about 2 *N*) was added carefully until the first definite color change occurred. The solution was then boiled for about two minutes to coagulate the precipitate and filtered into a platinum dish in which the filtrate was evaporated to dryness. After the careful expulsion of most of the ammonium salts, the residue in the dish was digested with concentrated hydrochloric acid and the solution and any undissolved residue were transferred to a weighed platinum crucible. After evaporation the residue was ignited and weighed. Correction was made for the residue obtained upon similar evaporation of the distilled water (about 0.0002 g for 200 cc) and for the nonvolatile matter contained in the added ammonium chloride (0.0002 g in 5 g). Since these corrections were of the same order of magnitude as most of the residues obtained, any of the latter less than 0.0002 g may be considered negligible. The results obtained are shown in Table 1.

TABLE 1

Precipitation of $Al(OH)_3$ by NH_4OH Using Various Indicators

[$AlCl_3$ solution equivalent to 0.10 g Al_2O_3, precipitated in a volume of 200 cc]

Experiment	Indicator	Color change [a] [H+]—approximate	NH_4Cl added g	Al_2O_3 in filtrate g	Remarks
1	Para nitrophenol	10^{-6}	5	0.0010	
2	.....do	10^{-6}	5	.0012	
3	Methyl red	$10^{-6.5}$	0	Appreciable.	Coagulated poorly.
4	.....do	$10^{-6.5}$	5	.0001	
5	.....do	$10^{-6.5}$	5	.0000	
6	Rosolic acid	$10^{-7.5}$	0	.0000	
7	.....do	$10^{-7.5}$	5	.0000	
8	.....do	$10^{-7.5}$	5	.0002	Macerated paper used.
9	Phenolphthalein	10^{-9}	0	.0004	
10	.....do	10^{-9}	5	.0004	

[a] The approximate points of color change selected were measured with the hydrogen electrode at room temperature.

From Table 1 it is evident that considerable aluminium hydroxide remains unprecipitated when the solution is just alkaline to para-nitrophenol, while a smaller amount, but still appreciable, is redissolved when the solution is just alkaline to phenolphthalein. So far as accuracy is concerned, there is no choice between the use of methyl red and of rosolic acid. Practically, however, methyl red has been found preferable, because of its sharper color change, and because the end point is reached while approaching neutrality; that is, a slight excess of ammonia is less likely to cause re-solution. Moreover, solutions just alkaline to methyl red are less likely to attack Jena or similar glassware than are solutions slightly alkaline to rosolic acid. In using methyl red, however, it is essential to have appreciable ammonium chloride present to facilitate coagulation. The fact that coagulation occurs more readily, even in the presence of only small amounts of ammonium chloride, when the solution is just alkaline to rosolic acid (that is, when $[H^+] < 10^{-7}$) would appear to indicate that the OH^- ion itself exerts a coagulating effect upon the colloid.

3. FACTORS AFFECTING THE FORM OF THE PRECIPITATE

Obviously, in actual analysis it is desirable not only to effect complete precipitation, but also to obtain the precipitate in a form that is readily filtered and easily washed. Such conditions are difficult to realize with a precipitated colloid, such as aluminium hydroxide. Numerous efforts have been made to devise conditions that will accomplish this end. In general, it has been recognized that while short boiling is desirable to effect coagulation, longer boiling renders the precipitate slimy and difficult to filter. As previously noted, the use of ammonium chloride is advantageous in producing the well-known salt effect in the coagulation of such a precipitate, as well as in reducing the actual solubility. These two factors were the only ones found to have a favorable influence upon the method of precipitation. The conclusion of W. E. Taylor,[12] that if the solution be heated to just 66° C before the addition of ammonia and subsequently boiled the precipitate is "granular," could not be confirmed by R. Sudgen [13] nor by the author. The recommendation of A. Guyard [14] to add glycerine to the solution before precipitating with ammonia was tried, and no improvement in the character of the precipitate was noted, while about 5 mg of Al_2O_3 were found in the filtrate. Similarly, the procedure of R. E. Divine,[15] viz, precipitation in the presence of tannic acid, while it produced an appreciable improvement in the character of the precipitate, yielded a filtrate containing from 1 to 5 mg of Al_2O_3, depending upon whether the solution was boiled for some time or was filtered after two minutes boiling.

While, therefore, it seems impossible to specify satisfactory conditions for the rapid filtration of considerable amounts of aluminium hydroxide, it is believed that for amounts up to 0.10 g Al_2O_3, the following conditions will yield fairly satisfactory results, viz: (1) The presence of at least 5 g of ammonium chloride in a volume of 200 cc; (2) addition of dilute ammonia to the nearly boiling solution until it is just alkaline to methyl red (or rosolic acid); (3) boiling for not more than two minutes; and (4) filtration without waiting long for the precipitate to subside. (In some cases the precipitate was found to settle quite readily; while in others it showed a tendency to rise to the surface and would not settle, even on long standing.) The addition of macerated filter paper before precipitation has been found advantageous in aiding filtration (and also ignition), especially of large amounts of the precipitate.

---

[12] Chem. News, 103, p. 169; 1911.

[13] Chem. News, 104, p. 35; 1911.

[14] Z. anal. Chem., 22, p. 426; 1883.

[15] J. Soc. Chem. Ind., 24, p. 11; 1905.

4. PRECIPITATION IN THE PRESENCE OF IRON

It is often necessary to precipitate ferric and aluminium hydroxides together. This can be accomplished readily by the procedure above recommended, since it was found that ferric hydroxide is completely precipitated by ammonia before the solution is alkaline to methyl red or to rosolic acid. In case sufficient iron is present to obscure the color of the indicator, it may be precipitated first by the careful addition of ammonia and caused to settle by short boiling, after which the color of the indicator can readily be recognized in the supernatant liquid and more ammonia added, if necessary, or any large excess of ammonia may be neutralized with dilute acid.

The writer has heard of an opinion (not published so far as known) that in the presence of ferric hydroxide the solubility of aluminium hydroxide in ammonia is decreased and that under such conditions there is less need for care in the addition of ammonia. Experiments have shown that this conclusion is unwarranted, since with any appreciable excess of ammonia considerable amounts of alumina were found in the filtrate even when large amounts of ferric hydroxide were present.

V. WASHING THE PRECIPITATE

In spite of the generally recognized fact that precipitates such as aluminium hydroxide readily assume the colloidal state when treated with pure water, many textbooks, even in recent editions, recommend the washing of aluminium hydroxide with hot water. That such a procedure is unsafe is readily seen from the fact that upon washing precipitates equivalent to 0.10 g Al_2O_3, with only 75 cc of hot water, from 0.5 to 2 mg of Al_2O_3 were found in the washings. The obvious remedy, viz, washing with a solution of a volatile ammonium salt, such as ammonium chloride or nitrate, has been suggested by numerous authors.[16] From the standpoint of the "salt" action there appears to be no preference between ammonium nitrate and chloride. The former has been used most frequently, partly because of its slight advantage in assisting combustion of the filter paper and partly because of the opinion still prevalent, though frequently disproven, that the presence of ammonium chloride during ignition would cause loss of alumina by volatilization of the chloride.[17] As pointed out by W. F. Hillebrand,[18] when the original solution contains chlorides and it is desired to evaporate the filtrate and washings in platinum and to expel ammonium salts, it is undesirable to use ammonium nitrate in the wash water, owing to attack of the platinum vessels. In the present research, therefore, a hot 2 per cent solution of ammonium chloride was used. In view of the fact that, owing to hydrolysis, solutions of ammonium chloride and ammonium nitrate are slightly acid to methyl red, it was at first assumed that, as suggested by Trautmann,[19] there would be an advantage in rendering such solutions slightly alkaline with ammonia. In practice, however, it was found that there was no appreciable difference in the amount of alumina dissolved by the "neutral" and the alkaline solutions, the residues obtained from 100 cc of the washings being almost invariably less than 0.3 mg. The use of solutions of the pure salts, with no addition of ammonia, is therefore recommended, especially as solutions rendered alkaline are more likely to act upon the glass of the wash bottle and thus to become contaminated.

VI. SEPARATION FROM OTHER ELEMENTS

In the separation of aluminium from other elements of the succeeding groups in the usual analytical procedure by precipitation with ammonia, three sources of contamination may be encountered: (1) Adsorption of various compounds by the precipitate; (2) co-precipitation of hydroxides which require a considerable excess of ammonia for re-solution; and (3) formation of insoluble carbonates by absorption of carbon dioxide from the air.

---

[16] Penfield and Harper, Amer. J. Sci., **32**, p. 107, 1886; W. Trautmann, Z. angew. Chem., **26** (aufsatz), p. 702, 1913; W. H. Daudt, J. Ind. Eng. Chem., **7**, p. 847, 1915.

[17] It has been shown by Daudt (J. Ind. Eng. Chem., **7**, p. 847, 1915) that 1 per cent ammonium chloride solution may be used for washing precipitates containing ferric hydroxide, with no loss of iron by volatilization.

[18] Bulletin 422, United States Geol. Survey, p. 99; 1910.

[19] Z. angew. Chem., **26** (aufsatz), p. 702; 1913.

The first effect is common, in some degree at least, to all the elements that may be present, the amount of a given element included in the precipitate being determined principally by its concentration in the solution, the character of the precipitate, and the method of washing. As previously pointed out, it has been found impracticable to precipitate aluminium hydroxide in any but a relatively gelatinous condition. It is obvious, therefore, that the only practical method of eliminating elements such as the alkalies, which are likely to be present in considerable amount in the solution, is to dissolve and reprecipitate. That such a procedure is quite efficient may be judged by the fact that from a solution containing 0.1000 g Al_2O_3 and 10 g of sodium chloride in a volume of 200 cc the precipitate obtained after a single precipitation and washing 10 times with 2 per cent ammonium chloride weighed 0.1071 g and contained much NaCl. A similar precipitate which was washed only 5 times, dissolved in hydrochloric acid, reprecipitated, and again washed 5 times weighed 0.1008 g and contained only a trace of NaCl.

The elements which introduce the second difficulty include zinc, manganese, nickel, and cobalt. It is well recognized[20] that the separation of aluminium from such elements by means of ammonia is unsatisfactory, since the alkalinity required for the resolution of their hydroxides is such as to cause appreciable solution of the aluminium hydroxide also. Moreover, it was found that even in solutions just alkaline to methyl red, oxidation and precipitation of manganese occurred so rapidly as to preclude a quantitative separation from aluminium. For such separations, therefore, other procedures—for example, the basic acetate method—must be employed.

The precipitation conditions above recommended have been found especially favorable in the separation from those elements such as barium, calcium, strontium, and, to a less extent, magnesium, whose carbonates are likely to be formed by absorption of carbon dioxide, and carried down by the precipitate. It has been found experimentally that in solutions containing barium and calcium, which are neutral or even slightly alkaline to rosolic acid—that is, $[H^+] = 10^{-7}$ to $10^{-7.5}$—it is impossible to form a precipitate of the carbonates by exposure to the atmosphere.[21] Aluminiumhydroxide precipitates obtained from solutions containing 0.1000 g Al_2O_3 and calcium and barium chlorides equivalent to 0.2 g CaO and BaO, respectively—that is, twice the amount of Al_2O_3—and washed 5 times with 2 per cent ammoniumchloride solution weighed 0.0998 and 0.0999 g, and were found to be free from calcium and barium.

---

[20] A. A. Noyes, W. C. Bray, and E. B. Spear, J. Am. Chem. Soc., **30**, pp. 482 and 532; 1908.

The beneficial effect of ammonium chloride in the separation of aluminium from magnesium has long been recognized. Formerly it was explained by the formation of a double salt, though more recently it has been attributed to the repression by the ammonium chloride of the alkalinity of the ammonium hydroxide to a point insufficient to precipitate the magnesium hydroxide.[22] The latter view is confirmed by the results of Hildebrand and Harned,[23] who found that Mg $(OH)_2$ is not precipitated until $[H^+]$ is less than 10^{-9}, and by the curves shown in Fig. 2 of this paper, in which the above effect of ammonium chloride is clearly shown. That the procedure recommended is effective in the separation of aluminium and magnesium is shown by experiments in which aluminium hydroxide equivalent to 0.10 g Al_2O_3, precipitated in the presence of magnesium chloride equivalent to 0.2 g MgO, contained less than 0.0010 g MgO.

VII. IGNITION AND WEIGHING OF THE PRECIPITATE

The principal questions involved in the ignition of the aluminium hydroxide are (1) the hygroscopicity of the ignited oxide; (2) the temperature and length of time required for dehydration; and (3) the effect of chlorides upon the ignition.

---

[21] This observation is approximately in accordance with the result obtained by calculating the alkalinity of barium chloride or calcium chloride solutions—for example, 0.1 *N*—saturated with respect to the neutral carbonates, in equilibrium with the normal atmosphere. (See J. Johnston, J. Am. Chem. Soc., **37**, p. 2001; 1915.) Thus the ionization of 0.1 *N* barium-chloride solution may be assumed as 70 per cent: that is, $[Ba^{++}]$ is 0.07. Since at 16° the solubility product $[Ba^{++}]\,[CO_3^{=}]$ equals 7×10^{-9}, the $[CO_3^{=}]$ in such a solution is equal to 10^{-7}. In any solutions at 16° in equilibrium with an atmosphere containing CO_2 with a partial pressure P, $\frac{[OH^-]^2}{[CO_3^{=}]}$ i. e. ${}^2[OH^-]^2 = \frac{3.4\times10^{-11}}{P}$. While the ordinary atmosphere contains about three parts of CO_2 in 10 000, the air in a laboratory may often contain five parts or more in 10 000. In such a case $P=5\times10^{-4}$, and therefore $[OH^-]=0.84\times10^{-7}$. If $K_{w18^\circ}=0.5\times10^{-14}$, then $[H^+]$ is about 0.6×10^{-7} or $10^{-7.2}$; that is, the solution must be slightly alkaline before any $BaCO_3$ can be precipitated by exposure to air containing the normal amount of CO_2. From similar calculations for 0.1 *N* $CaCl_2$, assuming that $[Ca^{++}]\,[CO_3^{=}]=0.98\times10^{-8}$, it may be shown that $[OH^-]=1.0\times10^{-7}$; or $[H^+]=0.5\times10^{-7}$ or $10^{-7.3}$ before any $CaCO_3$ will be precipitated upon exposure to the atmosphere. Moreover, such carbonates are prone to form supersaturated solutions and precipitation may not occur even at the points designated.

[22] J. M. Loven, Z. anorg. Chem., **11**, p. 404, 1896; F. P. Treadwell, Z. anorg. Chem., **37**, p. 326, 1903; W. Herz and G. Muhs, Z. anorg. Chem., **38**, p. 138, 1904.

[23] Orig. com., Eighth intern. cong. Appl. Chem., **1**, p. 217; 1912.

1. HYGROSCOPICITY OF ALUMINIUM OXIDE

The fact that ignited Al_2O_3 readily absorbs water has been recognized and pointed out by many authors.[24] This property has, in fact, been made the basis for the recommendation of the use of Al_2O_3 as a dehydrating agent.[25] It should be noted, however, that for the latter use the Al_2O_3 should not be strongly ignited. Many of the experiments that have been conducted to determine the hygroscopicity of such substances as Al_2O_3 have little bearing upon analytical procedures, since no distinction was made between the amount of water absorbed and the rate of absorption, especially during the first few minutes exposure. Tests at this Bureau have shown that in common with most substances capable of absorbing moisture (even those not intrinsically hygroscopic) recently ignited Al_2O_3 absorbs within the first 10 minutes exposure to the atmosphere a large proportion of the water which it will absorb in 24 hours. Since, as frequently pointed out, the atmosphere in an ordinary desiccator which has recently been opened is not greatly different from the atmosphere prevailing in the room, it is obvious that the all too common practice of placing in a desiccator ignited precipitates such as Al_2O_3 in uncovered crucibles, is likely to lead to even greater errors than those resulting during the period required for rapid weighing. That a well-fitting cover on a platinum crucible is efficient in preventing absorption of moisture in the desiccator or on the balance has been frequently demonstrated. Thus, a crucible containing 0.10 g ignited Al_2O_3, which when allowed to stand covered upon the balance showed no appreciable change in weight in five minutes, gained as much as 0.0010 g when uncovered for five minutes. For any accurate work in the determination of alumina, therefore, and especially in any experiments designed to test the temperature and period required for the ignition of such substances, it is absolutely essential that the crucible be well covered both in the desiccator and upon the balance.

2. TEMPERATURE AND TIME OF IGNITION

Directions for the ignition of alumina[26] have usually prescribed blasting for periods varying from 10 to 30 minutes, followed by successive short periods until constant weight is secured. While it is evident that in order to expel the last traces of moisture from such a precipitate, originally in a gelatinous condition, the use of a high temperature is desirable, it may be readily shown that long blasting is not necessary, at least for precipitates up to 0.2 g Al_2O_3. In numerous experiments with 0.1 g Al_2O_3 the total loss in weight produced by various periods of blasting following the first 5 minutes blasting was less than 0.0002 g. In order to show conclusively that dehydration is complete after 5 or 10 minutes blasting, at a temperature from 1100° to 1150° C, a covered crucible, of especially pure platinum, containing 0.7 g Al_2O_3, derived from three precipitates each of which had been blasted for 5 minutes, was again blasted for 5 minutes and placed in a vacuum sulphuric acid desiccator, which was quickly exhausted. After cooling, the crucible was quickly weighed against a tared crucible, and was then heated for three periods of 10 minutes each to a temperature of 1440° to 1460° in an electric furnace.[27]

---

[24] C. F. Cross, Chem. News, **39**, p. 161, 1879; Hess and Campbell, J. Am. Chem. Soc., **21**, p. 776, 1899; E. T. Allen and V. H. Gottschalk, Am. Chem. Jour., **24**, p. 292, 1900.

[25] F. M. G. Johnson, J. Am. Chem. Soc., **34**, p. 911; 1912.

[26] H. Moissan, Compt. rend., **121**, p. 851, 1895; P. H. Walker and J. B. Wilson, Chem. Eng., **16**, p. 159, 1912; W. H. Daudt, J. Ind. Eng. Chem., **7**, p. 847, 1915; and numerous textbooks.

The results of the experiments were as follows:

TABLE 2

Ignition of Al_2O_3

	Weight against tare
	Grams
Empty crucible	3.1665
Including Al_2O_3 (previously blasted but exposed in transfer)	3.8953
After five minutes blasting	3.8943
Weight of Al_2O_3	0.7278
After 10 minutes at 1440°-1460°	3.8943
After second 10 minutes at 1440°-1460°	3.8941
After third 10 minutes at 1440°-1460°	3.8940
Weight of empty crucible after brushing out precipitate	3.1662
Weight of Al_2O_3 after heating	0.7278

From these results it is evident that, making allowance for the loss in weight of the platinum crucible (0.0003 g), exposure to a temperature of over 1400° C produced no appreciable change in weight of Al_2O_3 previously blasted for not over 15 minutes.

From these results it is apparent that the continued losses in weight noted by some authors upon successive blastings of Al_2O_3 were probably due, not to further dehydration of the precipitate, but to losses in weight of the crucibles (which in commercial platinum may be quite appreciable); or, in case the crucibles were not covered while in the desiccator and on the balance, to a decrease in the hygroscopicity of the precipitate. In other words, at no time was the true anhydrous weight obtained, but always a weight including some amount of absorbed moisture, which amount decreases (and may become almost negligible) after the precipitate has been heated to high temperatures for a considerable period. Owing to the frequent failure to mention whether the crucibles were covered during the ignition and weighing, it is impossible to determine in which cases the above criticism applies. Such omissions indicate, however, a lack of appreciation of the importance of covering the crucibles.

---

[27] Thanks are due to R. B. Sosman and J. C. Hostetter, of the Geophysical Laboratory, for assistance in these high temperature experiments, conducted in 1912.

3. EFFECT OF AMMONIUM CHLORIDE UPON THE IGNITION

The still prevalent misconception that when aluminium hydroxide containing ammonium chloride is ignited, there is loss of aluminium, dates back at least to 1875.[28] It has been disproven so frequently [29] that it would be superfluous to dwell upon it were it not for the fact that it is referred to even in recent textbooks. The following experiments, while not essential to establish this, are perhaps of interest in still further demonstrating the absence of such an effect. Measured portions of a pure $AlCl_3$ solution were evaporated to small volumes in weighed platinum crucibles, after which pure ammonia in slight excess was added. Evaporation was continued to dryness and the residues were heated until all ammonium salts were expelled, and were finally blasted and weighed. The results, together with those obtained by the procedure recommended below (which had been found to give accurate results with metallic aluminium) are shown in Table 3.

TABLE 3

Experiment	Method	50 cc $AlCl_3$ yielded Al_2O_3
		Gram
1	Direct evaporation	0.0998
2	.....do	.0997
3	Precipitation	.1002
4	.....do	.1001
5	.....do	.1000
6	.....do	.0999

---

[28] C. R. Fresenius, Quantitative analysis, sixth Ger. edition; 1875.

[29] Allen and Gottschalk, Am. Chem. Jour., 24, p. 292, 1900; W. F. Hillebrand, Bull. 422, United States Geol. Survey, p. 99, 1910; W. H. Daudt, J. Ind. Eng. Chem., 7, p. 847, 1915.

From Table 3 it may be seen that in experiments 1 and 2, where the aluminium hydroxide was certainly in very intimate contact with an excess of ammonium chloride, any loss of aluminium by volatilization was so small as to be negligible. Moreover, the weights in experiments 3–6 include corrections for the filter ash and for known small impurities in the reagents and water, and are therefore probably somewhat less accurate than those obtained by direct evaporation.

VIII. PROCEDURE RECOMMENDED

From the foregoing considerations the following conditions are recommended for the determination of aluminium hydroxide. To the solution containing 5 g of ammonium chloride per 200 cc of solution, or an equivalent amount of hydrochloric acid, add a few drops of methyl red (0.2 per cent alcoholic solution) and heat just to boiling. Carefully add dilute ammonium hydroxide dropwise until the color of the solution changes to a distinct yellow. Boil the solution for one to two minutes and filter at once. Wash the precipitate thoroughly with hot 2 per cent ammonium chloride (or nitrate) solution. Ignite in a platinum crucible and after the carbon is all burned off blast for five minutes; cover the crucible and place it in a desiccator until cool. Weigh covered as rapidly as possible. A second blasting of five minutes is desirable, especially as it permits a more rapid weighing, and consequently probably more accurate results.

IX. CONFIRMATORY EXPERIMENTS

A weakness of many of the published researches upon the determination of aluminium is the lack of suitable standards by which to test the proposed methods. The use for this purpose of hydrated salts of possibly uncertain hydration, such as the alums, is not to be recommended for accurate work, and in the few cases where metallic aluminium has been used no detailed evidence of the purity has been presented. The following few experiments, though by no means exhaustive, appear to show that the method just described will yield results accurate to at least 1 part in 300 (which is more than sufficient for most purposes), and probably better.

Two samples of the purest aluminium that could be obtained in 1912 from the Aluminum Company of America were analyzed by the methods described by J. O. Handy,[30] yielding the following results for the only elements that could be detected,

TABLE 4

Analysis of Aluminium

Sample	A	B
	Per cent	Per cent
Silicon	0.13	0.16
Copper	.01	.01
Iron	.25	.17
Aluminium (difference)	99.61	99.66

Weighed portions (about 1.3 g) of these samples were dissolved in hydrochloric acid and the solutions were oxidized with a small amount of nitric acid and filtered to remove silicon. The filtrates were diluted to measured volumes and aliquots used for the determination of aluminium as above described, about 0.25 g of Al_2O_3 being weighed in each determination. The ammonia was redistilled and all reagents carefully tested and found free from appreciable contamination. The weights of precipitates were corrected for the filter ash and for the amount of Fe_2O_3 corresponding to the iron found by the previous analysis. The results are shown in Table 5.[31]

TABLE 5

Aluminium Determination in Metallic Aluminium

Experiment	Sample	Weight of sample	Found		Al	
			Al_2O_3	Al	Found	By difference
			g	g	Per cent	Per cent
1	A	0.1298	0.2445	0.1297	99.90	99.61
2	A	.1298	.2443	.1296	99.82	99.61
3	B	.1288	.2428	.1288	99.95	99.66

---

[30] J. Am. Chem. Soc., 18, p. 768; 1896.

[31] In calculating the weight of aluminium present in the Al_2O_3, the 1916 atomic weight of Al=27.1 has been used. It is at least interesting, though probably not significant with so few experiments, to note that if the round atomic weight 27 be used for Al the values for per cent Al found become, respectively, 99.73 and 99.67 for A and 99.78 for B—that is, they approach the amount found by difference, well within the experimental limit. No probable source of error in the determinations in Table 5 is likely to account for the existing discrepancies, amounting to from 0.0006 to 0.0008 g Al_2O_3. More experiments are required to throw light upon these discrepancies. The point is merely mentioned as of interest in connection with the statement of F. W. Clarke (Recalculation of the Atomic Weights, p. 268, 3d edition, 1910), that "the atomic weight of aluminium needs reinvestigation."

X. CONCLUSIONS

From the above experiments the following conclusions may be drawn, many of which simply confirm those of previous investigators:

(1) From observations made with a hydrogen electrode and with suitable indicators it was found that the precipitation of aluminium hydroxide by ammonium hydroxide is complete when $[H^+]$ is between $10^{-6.5}$ and $10^{-7.5}$, points approximately defined by the color change of methyl red and of rosolic acid.

(2) The presence of ammonium chloride during precipitation is advantageous in limiting the alkalinity and in coagulating the precipitate.

(3) Solutions of ammonium nitrate and chloride are equally satisfactory for washing the precipitate.

(4) The conditions of precipitation recommended are favorable for the simultaneous precipitation of aluminium and ferric hydroxides; and for their separation from calcium, strontium, barium, and magnesium.

(5) Crucibles containing ignited alumina should be kept covered in the desiccator and on the balance.

(6) For precipitates of from 0.1 to 0.2 g Al_2O_3 5 or 10 minutes blasting is sufficient.

(7) The presence of ammonium chloride during ignition causes no appreciable loss of alumina.

WASHINGTON, March 31, 1916.

CALCULATION OF PLANCK'S CONSTANT C_2

By J. H. Dellinger, Assistant Physicist

I. CALCULATION OF C_2 FROM ANY TWO OBSERVATIONS

The basis of a number of methods for measuring high temperatures is Planck's equation for radiation from a black body,

$$J=\frac{c_1}{\lambda^5\left(e^{\frac{c_2}{\lambda\theta}}-1\right)} \tag{1}$$

As this has been used very generally, much of the available data on properties of matter at high temperatures depend upon the physical constant c_2. This constant is important also in purely theoretical physics, in theories bearing on the constitution of the atom. The determination of the value of this constant is therefore of considerable interest.

Most of the determinations of c_2 have been from observations of the intensity of radiation J as a function of wave length λ, at constant temperature θ. Such observations were plotted in a curve with J as ordinates and λ as abscissas. c_2 was obtained by the method of equal ordinates; that is, by calculation from two wave lengths λ_1 and λ_2 corresponding to any pair of equal ordinates on opposite sides of the maximum (Fig. 1). The most convenient solution for this method was shown in a former paper[1] to be

$$c_2=\frac{\lambda_1\lambda_2\theta}{\lambda_2-\lambda_1}\left[5\log\frac{\lambda_2}{\lambda_1}-e^{-\frac{c_2}{\lambda_2\theta}}\right] \tag{2}$$

It is the purpose of the present paper to present a more general method of calculation which has several advantages.

---

[1] Buckingham and Dellinger, this Bulletin, 7, p. 393; 1911.

Since equation (1) contains two constants, it is obvious that two observations of J for any values of λ and θ suffice to find c_1 and c_2. Only c_2 is of interest, as c_1 merely gives the scale of ordinates, while c_2 determines the shape of the curve. It turns out that c_2 is calculable very simply from any two observations of J, λ, and θ. In particular, when the two observations are for the same temperature, c_2 is obtained from any two points on the J, λ curve by merely adding a term to the equation for equal ordinates, thus:

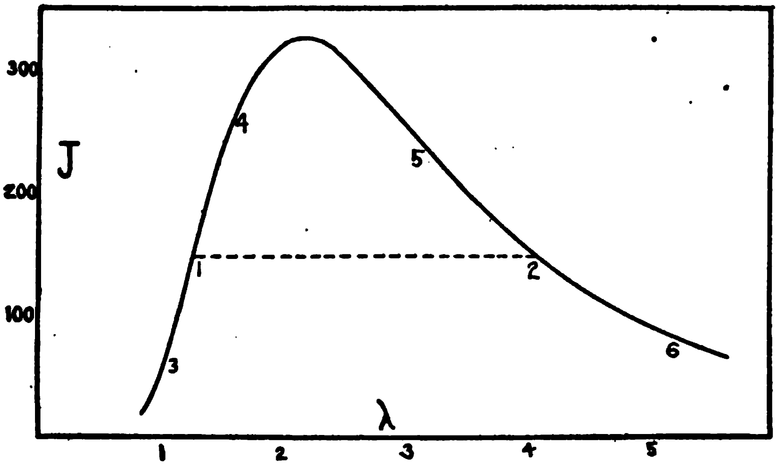


FIG. 1.—*Planck energy curve for 1350° K*

$$c_2 = \frac{\lambda_1\lambda_2\theta}{\lambda_2-\lambda_1}\left[\log\frac{J_2}{J_1} + 5\log\frac{\lambda_2}{\lambda_1} - e^{-\frac{c_2}{\lambda_2\theta}}\right] \qquad (3)$$

An explicit solution for c_2 has not been obtained, and would probably be complicated and useless if it could be found. A very valuable general expression is found as follows. Writing equation (1) in the form,

$$J_1 = \frac{c_1}{\lambda_1^5 e^{\frac{c_2}{\lambda_1\theta_1}}\left(1-e^{-\frac{c_2}{\lambda_1\theta_1}}\right)}$$

it follows that

$$e^{\frac{c_2}{\lambda_1\theta_1}} = \frac{c_1}{J_1\lambda_1^5\left(1-e^{-\frac{c_2}{\lambda_1\theta_1}}\right)}$$

$$\therefore \frac{c_2}{\lambda_1\theta_1} = \log c_1 - \log J_1 - 5\log\lambda_1 - \log\left(1-e^{-\frac{c_2}{\lambda_1\theta_1}}\right)$$

Writing the similar equation for J_2, λ_2, θ_2, and subtracting, we obtain

$$c_2 = \frac{\lambda_1\lambda_2\theta_1\theta_2}{\lambda_2\theta_2 - \lambda_1\theta_1}\left[\log\frac{J_2}{J_1} + 5\log\frac{\lambda_2}{\lambda_1} + \log\frac{1 - e^{-\frac{c_2}{\lambda_2\theta_2}}}{1 - e^{-\frac{c_2}{\lambda_1\theta_1}}}\right] \tag{4}$$

This equation contains c_2 in the right-hand member, but in a term which is always relatively small in practice. Since c_2 is a physical constant, a closely approximate value is known, which may be used in this term. A second approximation would rarely modify the result. This satisfactory solution may be simplified by introducing the relation

$$\log\left(1 - e^{-\frac{c_2}{\lambda\theta}}\right) = -e^{-\frac{c_2}{\lambda\theta}} - \frac{1}{2}e^{-\frac{2c_2}{\lambda\theta}} - \frac{1}{3}e^{-\frac{3c_2}{\lambda\theta}} - \ldots\ldots$$

When $\lambda_1\theta_1$ is not too close to $\lambda_2\theta_2$, the first term is sufficient, so that

$$c_2 = \frac{\lambda_1\lambda_2\theta_1\theta_2}{\lambda_2\theta_2 - \lambda_1\theta_1}\left[\log\frac{J_2}{J_1} + 5\log\frac{\lambda_2}{\lambda_1} - e^{-\frac{c_2}{\lambda_2\theta_2}}\right] \tag{5}$$

This equation is accurate enough for most purposes. It furnishes a very simple means of calculating c_2 from any two observations, there being no restriction to constant temperature or to constant wave length.

The possibility of obtaining a solution for c_2 in a form such as (5) has been indicated by C. N. Haskins.[3] He showed that c_2 could be expressed implicitly in terms of two observations of J, λ, θ, by means of the equation

$$x^n - Cx + C - 1 = 0 \tag{6}$$

where $x = e^{\frac{c_2}{\lambda_2\theta_2}}$ and $n = \frac{\lambda_2\theta_2}{\lambda_1\theta_1}$. Since n is not an integer, the equation is not solvable algebraically. Some tedious process such as successive approximations is necessary for a solution, so that the method is not as direct, convenient, or rapid as equation (5). Haskins pointed out that while previous methods for calculating c_2 depended upon the use of a plotted curve, the purely mathematical solution depends directly on the experimental data. All graphical errors are thus eliminated. While the graphical errors are smaller than the experimental errors at the present time, it is of interest to know that the former can be avoided.

Equation (5) is particularly interesting because all of the methods which have been used for the determination of c_2 may be derived from it very simply. In the first place, if the two observations are at constant wave length, $\lambda_1 = \lambda_2 = \lambda$, equation (5) gives at once:

---

[3] Physical Review, 3, p. 476; 1914.

$$c_2 = \frac{\lambda\theta_1\theta_2}{\theta_2 - \theta_1}\left[\log\frac{J_2}{J_1} - e^{-\frac{c_2}{\lambda\theta_2}}\right] \tag{7}$$

This is the equation for obtaining c_2 from an "isochromatic" curve; that is, observations at a fixed wave length. Isochromatics are used very widely in temperature measurement. In the second place, if temperature is kept constant instead of wave length, $\theta_1 = \theta_2 = \theta$, and equation (3) follows. Equation (3) represents the method which is discussed in detail in this paper. Thirdly, by placing $J_2 = J_1$ in equation (3), the method of equal ordinates appears. Fourthly, by omitting also the exponential correction term, Paschen's equation follows, viz,

$$c_2 = \frac{5\lambda_1\lambda_2\theta}{\lambda_2 - \lambda_1}\log\frac{\lambda_2}{\lambda_1} \tag{8}$$

Fifthly, an equation for the method used at the Reichsanstalt,[8] of observing the maximum J and the value of J at one other λ, follows from equation (3) by writing $\lambda_1 = \lambda$, $J_1 = J$, $\lambda_2 = \lambda_m$, $J_2 = J_m$,

$$4.965\frac{\lambda_m}{\lambda} - (4.965 - e^{-4.965}) = 5\log\frac{\lambda_m}{\lambda} + \log\frac{J_m}{J} \tag{9}$$

Having obtained λ_m, c_2 is given by the relation

$$c_2 = 4.965\,\lambda_m\theta \tag{10}$$

Equation (9) is transcendental, and in practice is solved by preliminary calculation of a table of J_m/J as a function of λ_m/λ. This method is inconvenient physically as well as mathematically. It requires observation of J at one particular point, the maximum of the curve; consequently, the method is impossible at all temperatures for which there is energy absorption at the maximum of the curve.

The chief interest attaching to equation (5) is its generality in relation to other equations, as just discussed. In determining c_2 from two observations, there is not necessarily any advantage in having both temperatures and both wave lengths different. In fact, the requirements of temperature measurement usually necessitate holding the temperature constant at least as long as the time required to observe two values of J. When the temperature is kept constant, and J observed as a function of λ, a so-called "isothermal" is obtained.

---

[8] Warburg, Leithäuser, Hupka and Müller, Ann. 345, p. 625; 1913.

In calculating c_2 from isothermals by the method of equal ordinates, it is necessary to draw a curve of J as a function of λ. One of the advantages of the mode of calculation of equation (3) is that no curve is required, and thus all the labor and the errors of plotting and reading a curve are eliminated. Since this method determines c_2 from any two points whatever on the Planck curve, it is applicable when only limited portions of the curve can be observed. This is an important consideration in practice, since absorption bands and other sources of error affect some parts of the curves, and it is sometimes impossible to find a usable ordinate on one side of the maximum equal to a certain ordinate on the other side. These difficulties have limited the general application of the previously used methods, but the two-point method is not affected by them.

Since the two-point method utilizes the observations directly, any abnormal point is very sharply shown up. If a point is in error, for instance, because of errors of observation or errors in the spectrometer setting, this is made evident by an abnormal value of c_2 resulting from the calculation. Each point stands by itself, whereas if a curve is plotted each point is necessarily affected by neighboring points. In the direct two-point calculation only the points affected by the experimental conditions will give wrong values of c_2. A point known to be normal can be used and various others combined with it, then any abnormal values are known to be due to the other points. The constancy of values of c_2 thus calculated from any desired pairs of points is a good criterion to show whether the observations follow Planck's law. Furthermore, variations of c_2 when thus calculated actually give an easy way of investigating the shape of the observed curve as compared with the Planck curve, without plotting either curve. Labor is thus saved, as it is desired to calculate the value of c_2 anyway for its own sake. Considerable information regarding the shape of the curve is given when the two points are both taken on the same side of the maximum, as shown in the example discussed below.

II. APPLICATION OF THE METHOD

The method was tried out on experimental data obtained by Dr. Coblentz, which he very kindly placed at the disposal of the writer. The data were from reliable observations, and the curve which was plotted from them gave consistent values of c_2 by the method of equal ordinates, with a mean very close to 14 360, practically identical with the general mean for all the curves obtained by Dr. Coblentz.[4] Certain of the calculations by the two-point method give values surprisingly different, as shown below. For convenience in calculation, equation (3) is used in the form

$$c_2 = \frac{2.3026\,\lambda_1\lambda_2\theta}{\lambda_2-\lambda_1}\left[\log_{10}\frac{J_2}{J_1}+5\log_{10}\frac{\lambda_2}{\lambda_1}-0.4343\,e^{-\frac{c_2}{\lambda_2\theta}}\right] \qquad (11)$$

When both points are at the right of the maximum, the exact formula

$$c_2 = \frac{2.3026\,\lambda_1\lambda_2\theta}{\lambda_2-\lambda_1}\left[\log_{10}\frac{J_2}{J_1}+5\log_{10}\frac{\lambda_2}{\lambda_1}+\log_{10}\frac{1-e^{-\frac{c_2}{\lambda_2\theta}}}{1-e^{-\frac{c_2}{\lambda_1\theta}}}\right] \qquad (12)$$

is used. When one of the points is at the left of the maximum, equation (11) is amply accurate.

In the exponential term in the equations, c_2 was taken equal to 14 350. The data were for a temperature of 1350°*K*, the theoretical curve for which is given in Fig. 1. Values of c_2 calculated by the method of equal ordinates from the observed curve agreed within 1 per cent, with a mean of 14 360. This agreement seemed a satisfactory indication that the data fit the Planck equation within the errors of experiment. The values were very closely checked by calculations from *nearly equal* ordinates, applying equation (11) to the actual observations. The first advantage of the two-point method appears here, viz, the same values of c_2 are obtained by direct calculation from nearly equal ordinates as by the method of equal ordinates, and the graph is dispensed with entirely.

When values of c_2 were calculated from a point of large ordinate on one side of the maximum and a point of small ordinate on the other side, as from points 3 and 5, or 4 and 6 (Fig. 1), there was a fair but not quite so good an agreement with the method of equal ordinates. Thus, the mean of seven such pairs of points gave 14 460.

When calculations were made from two points, both on the same side of the maximum, small departures from the theoretical curve had a magnified effect and very different values were found. Calculations made from nine pairs of points, such as 3 and 4, or 5 and 6 (Fig. 1), gave values of c_2 ranging from 14 530 to 14 930, with a mean of 14 750. These high values were found because the observed points were slightly below the theoretical curve in two regions, as discussed below.

---

[4] This Bulletin, 13, Scientific Paper No. 284; 1916.

For calculations from two points at the right of the maximum, equation (12) was used. Some of the calculations were made rigorously, using five significant figures in the intermediate steps. It was found, however, that the use of a slide rule gave the values of c_2 within 1 in the fourth figure; that is, well within the accuracy of observation. It may, therefore, be stated that these calculations can be made very rapidly, obtaining the logarithms and exponentials from tables and performing the multiplications by a slide rule. In calculating the values of c_2, as already stated, a preliminary value of $c_2 = 14\ 350$ was used in the term $e^{-\frac{c_2}{\lambda\theta}}$. A second approximation would make the values still greater. In the largest values, however, the increase would be only 5 in the fourth significant figure, and as this is within the experimental error the second approximation was not made.

It has been suggested to the author by C. E. Van Orstrand that the reason why the two-point method and the method of equal ordinates give different values is because they weight the observations differently; and that the only comprehensive solution would be by least squares, which would give every observation the proper weight. All of the methods which have been used for calculating c_2 are open to objection on this score. The two-point method, however, is the most powerful in indicating the shape of the curve. It also helps to locate any constant errors, and in this respect seems superior to the method of least squares, which assumes all departures from the theoretical to be accidental. This appears to be an important consideration at the present time, when there are so many variables affecting the observations. The method renders this very service in the case of the observations here discussed.

The excessively high values of c_2 obtained from points entirely on the left or entirely on the right of the maximum indicate that the observed points toward the left of each branch of the curve lie below the theoretical Planck curve. In other words, the curve is slightly sheared, but in such a way that its distortion does not appreciably affect the values calculated by the method of equal ordinates. As a result of this shearing, all the values of c_2 calculated from points on the same side of the maximum are either equal to or higher than the mean found by the method of equal ordinates, although the individual observations do not depart from the theoretical curve any more than can be accounted for by the large and unavoidable errors of observation. Thus a characteristic of the curve is disclosed by this method of calculation which would be overlooked when the calculations were made by equal ordinates.

It is not known whether this shearing of the curve is wholly a matter of experimental error or a true departure from Planck's equation. A similar characteristic of such curves was found at the Reichsanstalt;[5] that is, different values of c_2 were found from the left and the right sides of the curve (calculated as described above, from one point and *J* at the maximum). This behavior was found in curves obtained by using a fluorite prism. In the more recent work of Reichsanstalt, very consistent values of c_2 have been obtained, but a quartz prism is used and the observations are all on the left of the maximum, because quartz shows strong absorption at wave lengths above the maximum. It is impossible to say at the present time whether the abnormal values of c_2 obtained from the right side of the curve are due to the inadequacy of the theoretical formula or to the errors of observation.

It is worthy of note that the departures of the above observations from the theoretical curve come in that part of the curve where the Planck and the Wien equations give appreciably different values. In this region the observations fit the Planck law better than the Wien. In the regions of lower wave length and temperature where the two laws agree, they are well known to be very reliable. This is of the greatest importance in various methods of optical pyrometry, which are based on the Wien equation. The recent Reichsanstalt researches do not establish the validity of the Planck modification of the Wien equation, because that work was done in the ranges of wave length and temperature to which both equations apply. Coblentz has already pointed out[6] that the Planck equation has not received a thorough experimental verification. It may be seen from the calculations above that the two-point method shows the characteristics of experimental curves rather more vividly than any previously used criterion.

The Planck radiation equation has considerable importance in various theoretical fields, as well as in its direct experimental application. It is probably as valid to obtain the value of the Planck constant c_2 from its theoretical relations to other constants as from radiation data. Prof. Millikan, therefore, seems well justified in his suggestion[7] that a more precise value of c_2 is obtainable on the basis of photo-electric experiments than from radiation data, since higher precision is attained in the former experiments. Of course, the question of which data give the more accurate value could only be answered by an estimate of the constant errors in the two kinds of experiments.

---

[5] ZS Instrumentenkunde, **30**, p. 118; 1910.

[6] This Bulletin, **10**, p. 3; 1913.

III. DETERMINATION OF SPECIAL POINTS ON THE PLANCK CURVE

For certain points on a Planck isothermal curve, Wien's displacement law holds. The law is expressed by the equation,

$$c_2 = K\lambda_s\theta \tag{13}$$

where K is a constant and λ_s is the λ coordinate of the point. Such special points are the maximum of the curve, for which $K = 4.965$; the center of gravity, for which $K = 2.701$; and the points of inflection. By the use of the displacement law, c_2 could theoretically be obtained from an observation merely of the λ for one of these special points. As a matter of fact, however, none of these points can be taken directly from the curve with accuracy, so no additional ways of obtaining c_2 are really provided in this way. The earliest observers, such as Lummer and Pringsheim, did calculate c_2 from observations of λ at the maximum, but the method would no longer be considered. P. D. Foote has proposed[8] using the center of gravity similarly, obtaining the λ coordinate by mechanical integration of the curve. Such a method would involve all the errors of the curve and of the integration, the former being particularly formidable since a part of the curve known to be affected by absorption bands could not be omitted. Since only a finite portion of the curve can be integrated mechanically, a correction has to be computed by successive approximations. The method is laborious and not highly accurate, and is, in fact, not recommended by its author for actual use.

Not only are these special points unsuitable as means of determining c_2, but they may themselves be obtained most accurately and conveniently by the very process which is recommended in this paper for obtaining c_2. Any of the points for which the displacement law holds may be calculated from any two observed points. Substituting from equation (13) in equation (3), and letting $K = \frac{1}{K'}$

---

[7] Phys. Rev., 7, p. 378; 1916.

[8] This Bulletin, 12, p. 479; 1915.

$$\lambda_s = \frac{K'\lambda_1\lambda_3}{\lambda_2-\lambda_1}\left[\log\frac{J_2}{J_1}+5\log\frac{\lambda_2}{\lambda_1}-e^{-\frac{c_2}{\lambda_s\theta}}\right] \tag{14}$$

This is the same as equation (3), with K' substituted for θ. For the maximum of the curve, $K' = 0.2014$; for the center of gravity, $K' = 0.3702$. This means that the maximum of the curve need not be observed in order to determine it, and, in fact, it could not be determined with nearly as great accuracy by direct observation as by calculation from several pairs of reliable points. Also, the whole curve need not be observed in order to determine the center of gravity. Practically a single equation suffices to determine c_2 and all the special points from any two observed points.

It may be noted that only a very rough value of the temperature need be known in calculating the special points by equation (14). One additional possibility of the two-point method is, of course, the determination of temperature. Solving equation (3) for θ instead of for c_2,

$$\theta = \frac{c_2(\lambda_2-\lambda_1)}{\lambda_1\lambda_2\left[\log\frac{J_2}{J_1}+5\log\frac{\lambda_2}{\lambda_1}-e^{\frac{-c_2}{\lambda_2\theta}}\right]} \tag{15}$$

This requires knowledge of the value of c_2 and a roughly approximate value of θ. This would be a more accurate method of temperature measurement than the use of the displacement law for the maximum of the curve. It might be a useful method in certain experiments where the proper apparatus was set up.

IV. SUMMARY

The constant c_2 of Planck's radiation equation has heretofore been obtained from radiation data by processes involving the use of a graph. It may be determined very simply and directly from two observations at any wave lengths and temperatures. The formula for the case of constant temperature is only slightly different from the familiar equation for equal ordinates. The method eliminates all graphical difficulties, and is less limited by experimental conditions such as absorption bands in the air and the prism.

A mathematical discussion has been given, showing how very simply the equations for all the known methods of calculating c_2 may be deduced from a general solution of Planck's equation.

On applying the general method of calculating in terms of two points to an experimental energy curve, the power of the method in investigating the shape of the curve is strikingly shown. The departures of the observations from the Planck law are more vividly indicated than in other methods of calculation. The departures of individual points and of limited portions of the curve from the theoretical values stand out by themselves.

Points on the Planck curve for which Wien's displacement law holds, in particular the maximum of the curve, have been considered as furnishing additional ways of determining c_2. Such methods are debarred by lack of accuracy and, in fact, these special points may themselves be obtained most accurately and conveniently by the very process which is recommended in this paper for obtaining c_2. Substantially the same simple equation suffices to determine c_2 and all the special points.

WASHINGTON, May 10, 1916.

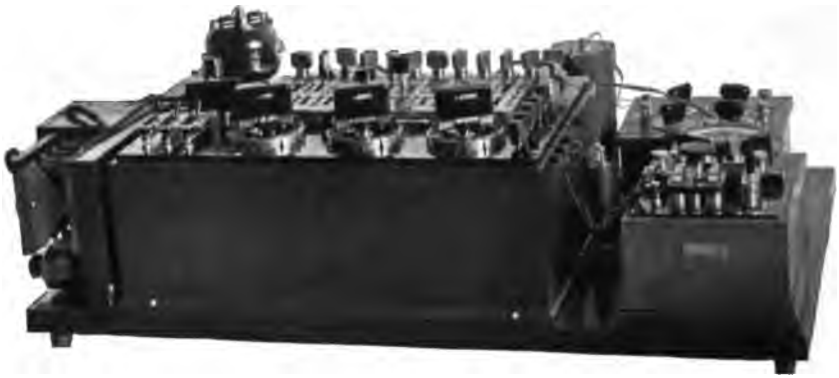


FIG. 1.—*Bridge arranged for oil immersion and automatic temperature control.* (*Bridge top measures 27 by 39 cm.*) *View also shows commutator, milliammeter for measuring current through bridge, etc.*

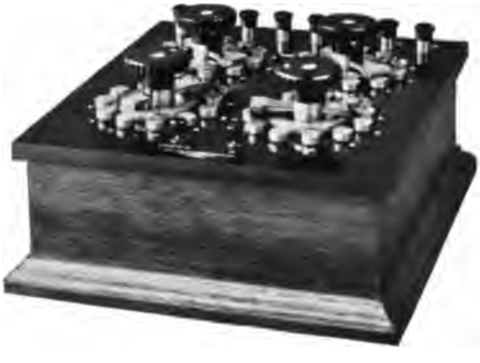


FIG. 2.—*Simple bridge without temperature control.* (*Bridge top measures 28 by 25 cm.*)

WHEATSTONE BRIDGES AND SOME ACCESSORY APPARATUS FOR RESISTANCE THERMOMETRY

By E. F. Mueller

CONTENTS

	Page
1. Type of bridge required	547
2. Improved slide-wire bridge	548
3. Bridge with shunt decades	548
(a) Shunted decades	549
(b) Adjustment of ratio arms	550
(c) Temperature control	550
(d) Effect of contact resistances	551
(e) Performance	552
4. Dial bridge	553
5. Bridge without temperature control	554
6. Measurement of potential terminal resistances	556
7. Interchanger for connecting several thermometers	558
8. Notation	560
9. Summary	561

1. TYPE OF BRIDGE REQUIRED

A type of Wheatstone bridge which has been found to meet practically all the requirements of precision measurements with resistance thermometers is one having equal ratio arms of rather high resistance (100 ohms or more) and a variable resistance arm of about 100 ohms, variable by steps of 0.0001 ohm. Such a bridge has recently been described.[1] Coils of 0.1 ohm (or even 0.01 ohm) and larger may be connected to mercury contact blocks and short-circuited by suitable amalgamated links. For resistances smaller than 0.1 ohm it is preferable to use a shunting arrangement, as described in the paper referred to [2] or, in some instances, a slide wire may be used. Plug or dial contacts should not, in general, be used directly in series with the variable arm as the variation in such contacts is of the same order of magnitude as the value of the smallest step.

---

[1] This Bulletin, 11, p. 571; 1915.

[2] Loc. cit., p. 572.

2. IMPROVED SLIDE-WIRE BRIDGE

A consideration of the ordinary bridge diagram, Fig. 3, in which *ab* and *ac* are the equal ratio arms, shows that resistance may be transferred to or from the remaining arms at three points: (1) By moving *d* along *bdc*, which is essentially the plan used in the Callendar-Griffiths bridges[8]; (2) by moving *b* along *dbg;* and (3) by moving *c* along *dcg*. In (2) and (3) the bridge balance is not independent of the resistance of the moving contact as in (1), but the effect of variations of this contact may be reduced to any desired extent by increasing *ab* and *ac* with which the contacts are in series.

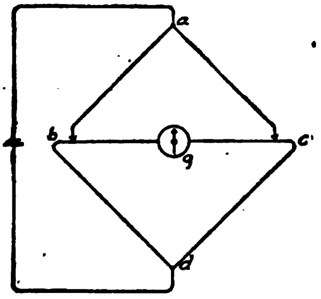


FIG. 3.—*Wheatstone bridge diagram*

The method just described may be used to introduce the 1-ohm decade and the 0.1-ohm decade, a row of 1-ohm coils between contact blocks being connected along *bg* and a row of 0.1-ohm coils along *gc*, the moving points *b* and *c* being either plugs or dial switches.

The above method was described by the writer several years ago to Mr. Leeds, of the Leeds & Northrup Co., and since that time has been used by them in their calorimetric bridges, the steps smaller than 0.1 ohm being secured by the use of a Kohlrausch slide-wire.

3. BRIDGE WITH SHUNT DECADES

Instead of a slide-wire, the smaller steps may also be obtained by the use of shunts. A bridge of this type was designed early in 1913 and has been in use for about two years. The general scheme of connections is shown in Fig. 4. There are two ratio coils of 250 ohms each and these are connected by a short (5 cm) slide-wire, which is used in adjusting them to equality. The ratio coils terminate in long bars which may be connected by means of plugs to the contact blocks of the 1-ohm and 0.1-ohm decades. The 10-ohm coils are connected to binding-post blocks and the desired number of coils are introduced into the circuit by making connection to the appropriate binding post. This method of connection is satisfactory in most instances, but may prove a source of inconvenience when considerable changes in the resistance to be measured are encountered, as may be the case when several thermometers are to be measured successively with the same bridge. If this decade is to be much used, it is desirable to make it a plug decade or, perhaps better, to use mercury contacts.

---

[8] H. L. Callendar, Phil. Mag. V, 32, p. 104, 1891; E. H. Griffiths, Nature, 53, p. 39, 1895.

(*a*) *Shunted Decades.*—In choosing the values for the shunted coils the formula for resistance of coils in parallel was put in the following form: If a resistance r is shunted by a resistance R, the effect of the shunt is to reduce r by an amount $\frac{r^2}{R+r}$. In the shunt decades—for example, the 0.01-ohm decade—R is given a series of values such that $\frac{r^2}{R+r}$ successively assumes the values 0.10, 0.09, 0.08—0.00; that is, successive values of R are defined by the equations $R+r=\frac{r^2}{0.10}$, etc., to $R+r=\frac{r^2}{0.00}$. Consequently to secure even-valued coils a value was sought for r^2, which should contain the factors 7 and 9 and therefore be divisible by all numbers below 10. The value $r^2=1.26$ was found to lead to suitable values for the coils of the 0.01-ohm decade. By making r_1 for the 0.001-ohm decade equal to $r/\sqrt{10}$ the successive values of R for this decade are made to differ by a constant amount from the values of R for the 0.01-ohm decade so that the corresponding coils for the two decades, with two exceptions, will be equal. The values of the shunted and shunting coils for the three decades are given in Table 1.

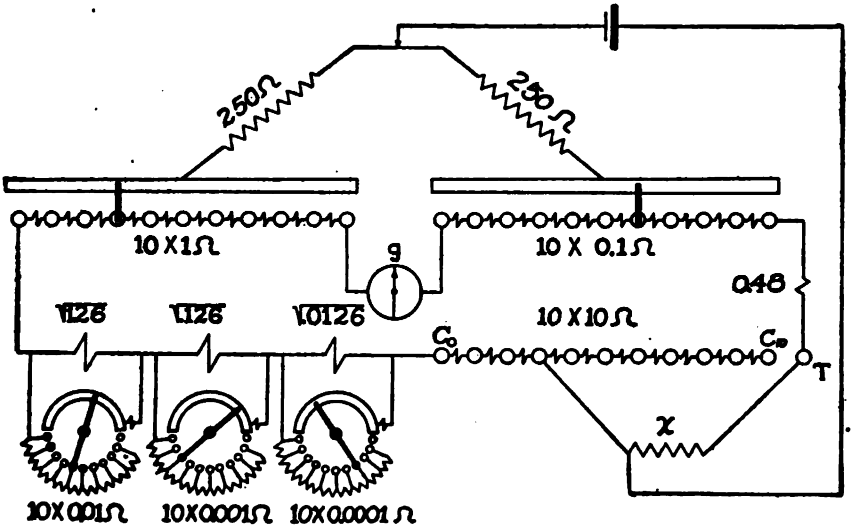


FIG. 4.—*Diagram of connections for bridge with shunt decades*

TABLE 1

Resistances of Shunted and Shunting Coils for Last Three Decades

Position of switch	Resistances in ohms			
	0.01-ohm decade—shunted coil, $\sqrt{1.26}=1.1225$		0.001-ohm decade—shunted coil, $\sqrt{0.126}=0.3550$ Individual coils	0.0001-ohm decade—shunted coil, $\sqrt{0.0126}=0.1122$ Individual coils
	Total shunting resistance	Individual coils		
0	$12.6-\sqrt{1.26}$	11.478	12.245	12.49
1	$14.0-\sqrt{1.26}$	1.4	1.4	1.4
2	$15.75-\sqrt{1.26}$	1.75	1.75	etc.
3	$18.0-\sqrt{1.26}$	2.25	etc.	
4	$21.0-\sqrt{1.26}$	3.0		
5	$25.2-\sqrt{1.26}$	4.2		
6	$31.5-\sqrt{1.26}$	6.3		
7	$42.0-\sqrt{1.26}$	10.5		
8	$63.0-\sqrt{1.26}$	21.0		
9	$126.-\sqrt{1.26}$	63.0		
10	$\infty-\sqrt{1.26}$	∞		

Instead of the number 1.26, other values may be found more suitable under some circumstances. For example, if it were required that the resistance of the three decades, with switches on zero positions, should be less than 1 ohm, the three shunted coils might be given the values $\sqrt{0.6048}$, $\sqrt{0.06048}$, and $\sqrt{0.006048}$ $(6048=7\times9\times96)$.

(*b*) *Adjustment of Ratio Arms.*—The slide-wire between the ratio coils is mounted inside the bridge in a vertical position and the slider is moved by turning a screw which engages the nut on which the slider is mounted. The head of this screw projects through a hole in the bridge top. The bridge is so arranged that the ratio coils may be interchanged at any time, but as this involves manipulating both plugs it is more convenient to adjust the coils to equality as often as may be necessary and not to interchange ratio coils during measurements. The accuracy with which this adjustment can be made is limited only by the sensitivity of the galvanometer used, and errors due to inequality of the ratio coils may therefore be made absolutely negligible.

(*c*) *Temperature Control.*—The bridge is mounted in an oil bath and thermostatic control of the temperature is provided for. The motor for circulating the oil is mounted on the bridge top and drives a screw propeller working in a vertical tube which also contains a heating coil. The oil is circulated downward through the tube, along the bottom of the box under a false bottom, thence upward and past the coils and through the tube again. A liquid-in-glass thermoregulator is mounted on the lower side of the false bottom. Power for operating the thermostat is supplied from the 110-volt alternating-current line, through a small (40-watt) transformer, which gives voltages up to 16 by steps of 1 volt. This transformer furnishes power for operating the motor and relay and for the heating coil. A switch is so connected that the high voltage can be applied to the heating coil for rapid heating to 30°, at which temperature the thermoregulator is set to operate. A buzzer, also operated from the transformer, indicates when the temperature of 30° has been reached.

A copper coil similar to the sealed coils used for the 10-ohm and 1-ohm decades mounted in the bridge and arranged so that its resistance can be measured with the bridge, shows that in such coils the fluctuations in the temperature of the oil, as the regulator operates, are almost completely damped out.

(*d*) *Effect of Contact Resistances.*—In order to make an estimate of the precision attainable with such a bridge it is necessary to assume the probable variations in the resistances of various kinds of contacts. For this purpose the following figures for the variation of various types of contacts when kept in good condition and correctly manipulated will be used:

Type of contact:	Probable variation
Binding post	0.00002 ohm
Plug	.0001 ohm
Switch	.0002 ohm

The figures quoted can not from the nature of the case be accurate, but they were the best estimates obtainable for the variations in well-made contacts. Granting that a contact of any of the three types will maintain a constant resistance—for example, to 1 microhm, for a short time if not disturbed—values will be computed for the bridge under consideration.

In measuring a resistance of about 25 ohms—for example, in a calorimetric experiment—the effect of any variation of the two plug contacts is only one-tenth of what it would be if these contacts were in the variable arm. Similarly, the maximum effect of variations in the dial switches is only one one-hundredth of the variation of one switch contact. Consequently the total error in the measurement due to contact resistances (the contacts on the binding posts may be left undisturbed) is that due to one or two plugs (reduced 10 times) and one switch (reduced 100 times), the total amounting to less than 20 microhms, a value comparable with that obtainable with a good mercury contact bridge.

If the resistance to be measured is about 2.5 ohms and is provided with potential terminals and measured in the manner to be described later, the effects of the variations in the plug contacts are reduced 100 times. The total effect of contact resistances in this case will therefore amount to less than 10 microhms, which is as good as can usually be attained with a mercury contact bridge.

The above figures may be summarized in the statement that the precision attainable in the use of the bridge is limited by the contact resistances in series with the ratio coils to about 1 part in 2 000 000 and in the measurement of low resistances is limited by the contact resistances in series with the shunts to about 0.000002 ohm.

The effects of thermoelectromotive forces at the moving contacts are also reduced to such an extent as not to be a source of inconvenience in making measurements.

(*e*) *Performance.*—Tests made with the bridge showed that readings consistent to 1 or 2 microhms could be made on resistances up to 10 ohms, thus indicating that at the time the tests were made the contacts were somewhat better than estimated above. The 1-ohm and larger coils are of the sealed type formerly described[4] and have during two years shown no changes amounting to more than 2 parts in 100 000. The bridge was made by O. Wolff and has proven satisfactory in all respects. A photograph of this bridge forms Fig. 1 (frontispiece).

In this bridge the decade arrangement is used exclusively, and the question may arise as to whether the calibration can be made as accurately as in the bridges in which the 5, 2, 2, 1 combinations are used. There is, of course, an accumulation of errors in each decade, reaching a maximum at the middle of the decade. Such errors could be avoided by comparing groups of coils, but as a matter of fact, in calibration, such high sensitivity may be secured and utilized if the contacts are in sufficiently good condition, that it is sufficient to evaluate each coil separately and add the values. It is worth noting that the decade plan is less subject to error in measuring changes of resistance, as is always done in resistance thermometry. For example, using the 5, 2, 2, 1 arrangement, it is necessary to change all coils if the resistance measured changes from 4 to 6 ohms, while with the decade arrangement it is only necessary to add the two coils which are equivalent to the change to be measured.

---

[4] This Bulletin, loc. cit., p. 575.

Successive independent calibrations show that the errors occurring in calibration are not of importance.

The bridge may be calibrated in international ohms without the use of precision auxiliary apparatus (except a standard coil), since by the use of an external variable resistance, each coil of a decade may be compared (by substitution) with the sum of the 10 coils of the next lower decade.[5]

4. DIAL BRIDGE

Another bridge of this general type but improved in details has been designed and constructed. It differs from the one already described principally in employing switches instead of plugs for the 1-ohm and 0.1-ohm decades, and in making the 10-ohm decade usable as a plug decade, or permitting connection directly to the

---

[5] For convenience the following account of the usual methods employed in such calibrations is added:

The coils in a decade will be designated as 1, 2, . . . 8, 9, x; so that 9 denotes the sum of the first nine 1-ohm coils and x denotes the sum of the ten 1-ohm coils, and similarly 0.x denotes the sum of the ten 0.1-ohm coils.

The calibration consists of the following steps:

1. Adjust the ratio coils to equality.
2. If a 10-ohm standard is used, measure this standard (preferably by using a commutator) in terms of the x coils, just as a resistance thermometer would be measured. From this a relation $x = 10 + \Delta$ international ohms is obtained.
3. Connect an external resistance variable by steps of 1 ohm, or preferably, 0.1 ohm to the bridge as for a resistance measurement.
4. Measure a resistance of approximately 1 ohm, first with l_1, and then with 0.x in the variable arm of the bridge, balance in each case being obtained by using the lower decades of the bridge.
5. Measure a resistance of approximately 2 ohms, first with $l_1 + l_2$ and then with $l_1 + 0.x$ in the variable arm, and continue this process up to 10 ohms.

From the observations under (4) and (5) the following equations are obtained:

$$l_1 + a_1 = 0.x + b_1, \text{ etc., to } l_x + a_x = 0.x + b_x.$$

a and b being the readings of the lower decades of the bridge necessary to obtain balance.

Adding the above equations gives

$$x + \Sigma a = 10[0.x] + \Sigma b$$

whence

$$0.x = 1 + 0.1[\Delta + \Sigma(a - b)] \text{ international ohms} = 1 + k.$$

Returning to the original equations we obtain

$$l_1 = 1 + k + b_1 - a_1, \text{ etc., to } l_x = 1 + k + b_x - a_x.$$

Finally the values so obtained are combined to give

$$1 = l_1;\ 2 = l_1 + l_2, \text{ etc., to } x = l_1 + l_2 + \ldots\ldots l_x.$$

A partial check on the arithmetical work is afforded by the fact that the value for x as finally obtained must be equal to $10 + \Delta$ ohms.

The calibration of the 0.1-ohm decade proceeds in the same way, the value of 0.x having already been obtained.

It is desirable to carry the observations and computations to one or two decimal places further than the number to be retained, to avoid the effect of the accumulation of errors which occurs in adding the values for the separate coils.

Since resistances variable by sufficiently small steps are not available for calibrating the lower decades, a slide wire may be used in the manner described in this Bulletin (11, p. 586, 1915). No elaborate arrangement is required, a manganin wire about 15 cm long and 1 mm in diameter fastened at the ends and provided with a movable clip for the battery connection being all that is required. The last decade is tested by means of galvanometer deflections.

As the relative accuracy required in the 0.01 ohm and lower decades is not high, calibration of these decades would be necessary only at intervals of several years.

coils through binding posts. The scheme of connections is essentially that of Fig. 4. A plan of this bridge differing very slightly from the one actually constructed is shown in Fig. 5. Mercury contacts could be substituted for the plug contacts without change of arrangement. An arrangement is provided for interchanging the ratio coils which can be used to adjust these coils to equality by means of the slide-wire. This adjustment may be made as follows: By connecting the post marked *T′* with one of the *C′* posts—for example, *C′* 40, and connecting *tc* to *C′* 20—the first two of the 10-ohm coils may be balanced against the second two. Then on shifting the switches of the 1-ohm and 0.1-ohm decades from the zero positions to *R*, the ratio coils are interchanged and the bridge balance will be disturbed unless the two are equal. If the coils are not equal, adjustment may be made by means of the slide-wire until no change in balance is noted on interchanging the ratio coils. A special stop with a release ordinarily prevents moving the switchs to the positions *R*.

The three keys are connected in the battery circuit and so arranged that the key *E* closes the circuit through an external resistance connected between the posts marked *E*, the 100 000 key closes the circuit through 100 000 ohms and the *o* key, through no added resistance.

5. BRIDGE WITHOUT TEMPERATURE CONTROL

The bridges so far described are designed for work of very high precision, and thermostatic control of the temperature is practically necessary to secure the accuracy for which the bridges were designed. In a large number of instances, however, a lower degree of precision is permissible. A bridge has recently been designed for measurements of such accuracy as is attainable without thermostatic control of coil temperature. With manganin coils of the average grade, measurements can be made to about 1 part in 25 000 if the coil temperatures are known within 1° or 2°, and the indications of a mercury thermometer with its bulb near the coils should give the coil temperatures within this limit. The bridge, which is designed largely for use with thermometers having a fundamental interval of 1 ohm, has four dial decades, the arrangement of the 1-ohm and 0.1-ohm decades being similar to those in the bridges already described, while the 0.01 and 0.001-ohm decades are secured by the use of shunts. There are also three 10-ohm coils connected to binding posts, so that the bridge

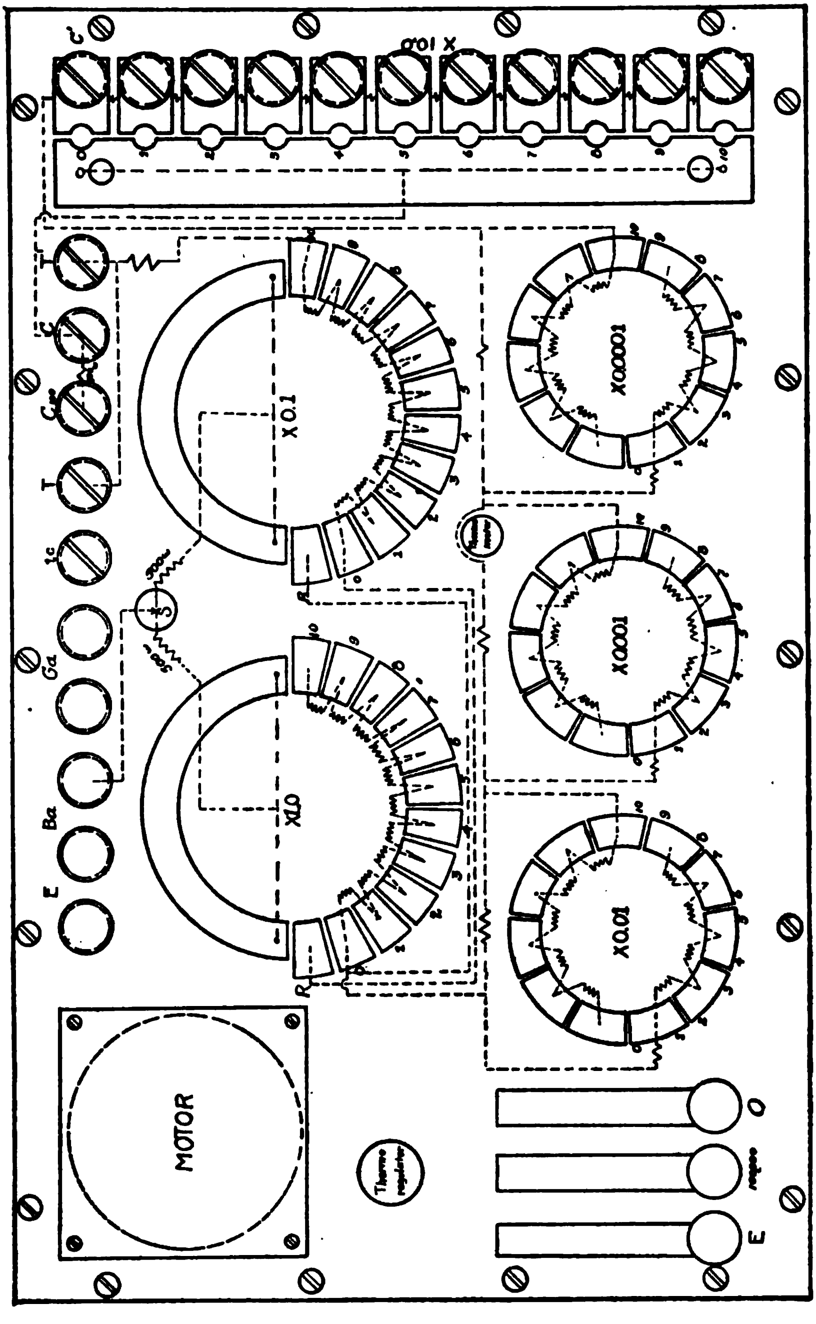


FIG. 5.—*Plan of dial bridge. (Switches not shown. Bridge top measures 24 by 39 cm.)*

has a range up to about 40 ohms, the smallest step being 0.001-ohm, and by utilizing galvanometer deflections readings to 0.0001 ohm may be made.

A bridge of this type has been made for the Bureau by the Leeds & Northrup Co. A photograph of it is shown in Fig 2. It has the advantages of compactness, portability, and simplicity. It will be necessary in some uses of the bridge to take into account the temperature coefficients of the coils in making calculations.

The possibilities of such a bridge may be seen from the following: An accuracy of 1 in 25 000 in resistance measurement corresponds to an accuracy of 0°.002 at −190°, about 0°.01 at room temperatures, about 0°.03 at 500°, and about 0°.05 at 1000°.

By adding another decade giving steps of 0.0001 ohm, this bridge would also be made suitable for calorimetric measurements of high precision, when used with a calorimetric thermometer of 10-ohms fundamental interval. In such measurements the actual temperature of the coils is not of importance, but it is very essential that the temperature remain constant at least to 0.1° during the short time required for an experiment.

A five-dial bridge of this type, which has essentially the arrangement shown in Fig. 4, has been made for the Bureau by the Leeds & Northrup Co.

A resistance thermometer having a fundamental interval of .1 ohm is best adapted for use with a bridge of this type over a wide range of temperature, since the 10-ohm decade is not required, and the resistance is sufficiently high, especially if the potential terminal type is used (see below) to permit readings to the accuracy stated above.

6. MEASUREMENT OF POTENTIAL TERMINAL RESISTANCES

The advantages of thermometers with potential terminals over those which depend upon a compensating method for eliminating lead resistances are too obvious to require discussion. The resistances of such thermometers may be measured with the bridges described in this paper by the method illustrated with reference to Fig. 6*a*. If r_1 and r_2 are the equal ratio arms and the bridge is balanced, the following relation holds

$$R_1 + C = X + T,$$

C and T being the "current" leads. If now T be connected to R and C to r_2 and the battery connected to t, a second balancing gives the relation

$$R_2 + T = X + C.$$

Combining the two equations gives $X = \frac{R_1 + R_2}{2}$.

This method can not be used with a slide-wire bridge of the Callendar-Griffiths type.

In practice the interchange described is effected by the use of a mercury commutator, as shown in Fig. 6*b*. The use of such a commutator involves the introduction of connecting resistances *a* and *b*. It is evident, however, that if two resistances be measured successively, the difference between these resistances will be determined correctly, as the difference of the two values found. One of the two resistances may be equal to zero. The points of the commutator to which *C* and *T* are connected are therefore also connected to contact blocks, which may be short-circuited by a plug, the battery connection being also made to the plug at the same time. Since in this case the two potential terminals coincide, the resistance so measured must be equal to zero. Consequently, the difference between the bridge reading obtained in this way (zero balance) and the reading obtained in measuring the resistance of the thermometer will be the resistance of the latter.

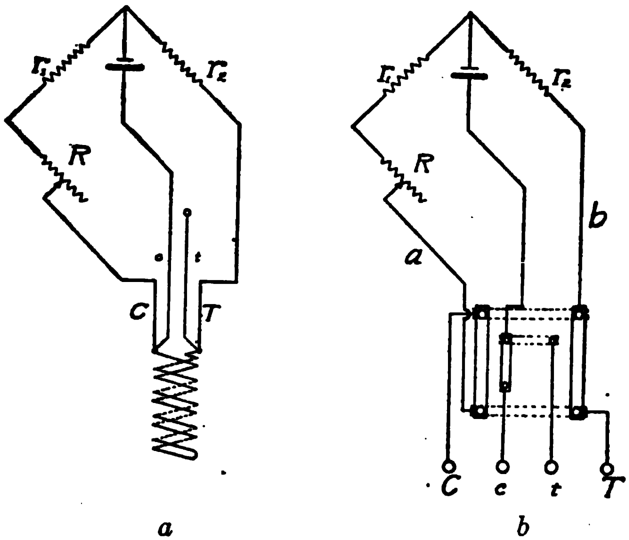


FIG. 6.—*Diagrams to illustrate method of measuring a potential terminal resistance with the Wheatstone bridge*

It should be noted that the value obtained for the resistance of the thermometer is independent of the connections *a* and *b*, and also independent of the resistance of the plug. It will, however, be affected by variations in the mercury contacts of the commutator.

The method described above was used by H. C. Dickinson and the writer in 1911, and has already been described by F. E. Smith[6] and by D. R. Harper, 3d.[7] A method of measuring the resistance of a four-terminal conductor by a simple bridge method using a commutator had previously been described by Edwards.[8]

In Fig. 7 is shown the plan of a commutator with the necessary binding posts, etc., for making the connections to the bridge and to the thermometer. With the commutator in the normal (*N*) position the connections are those of Fig. 6*a*. For determining the "zero balance," the commutator is used in the positions "*NZ*" and "*RZ*." It is desirable to have the connecting resistances so adjusted that the bridge balances for "*NZ*" and "*RZ*" are practically identical and the same as the balances obtained when a zero resistance is connected to the binding posts to which the thermometer is to be connected.

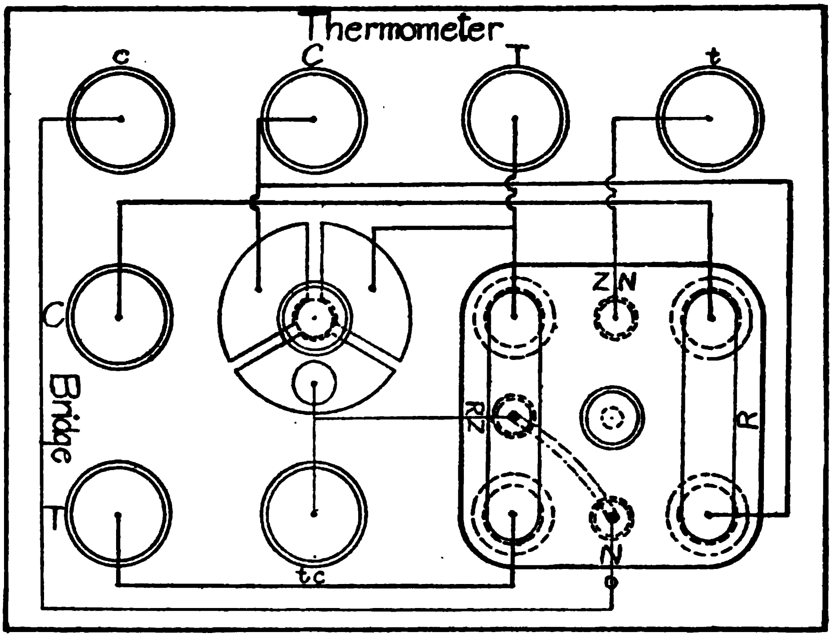


Fig. 7.—*Plan of commutator.* (*Scale full size.*)

7. INTERCHANGER FOR CONNECTING SEVERAL THERMOMETERS

In many instances—for example, in intercomparisons of thermometers—it is desirable to measure the resistances of a number of thermometers successively with a single bridge. This may be done without the necessity of connecting and disconnecting the thermometers by means of the arrangement shown in Fig. 8, which is arranged for four thermometers, of which those not in use are short-circuited by the mercury contact links. A separate switch makes the appropriate battery connections. Such a set of contact blocks may obviously be employed in connection with a commutator as described above. Fig. 9 shows the plan of an interchanger of this kind which is arranged to take four thermometers. The 5-point switch makes the necessary battery connections, the zero position giving the correct connections for the "zero balance." The inside row of binding posts and the switch are mounted above the level of the top, on hard-rubber blocks. The connecting resistances should be adjusted as for the simple commutator described above. With such an arrangement it is possible to measure in rapid succession with a single bridge, and without changing any connections, thermometers of the Callendar compensated type, the Siemens type, and the potential-terminal type.

---

[6] Phil. Mag., VI, 24, p. 554; 1912. [7] This Bulletin, 11, p. 296; 1915. [8] Proc. Am. Acad., 40, p. 549; 1905.

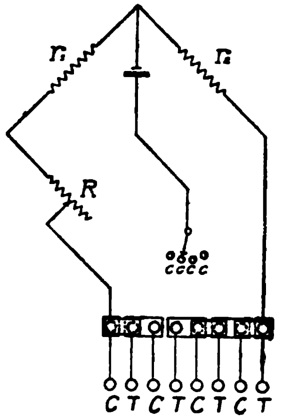


FIG. 8.—*Bridge diagram to illustrate method of connecting several thermometers*

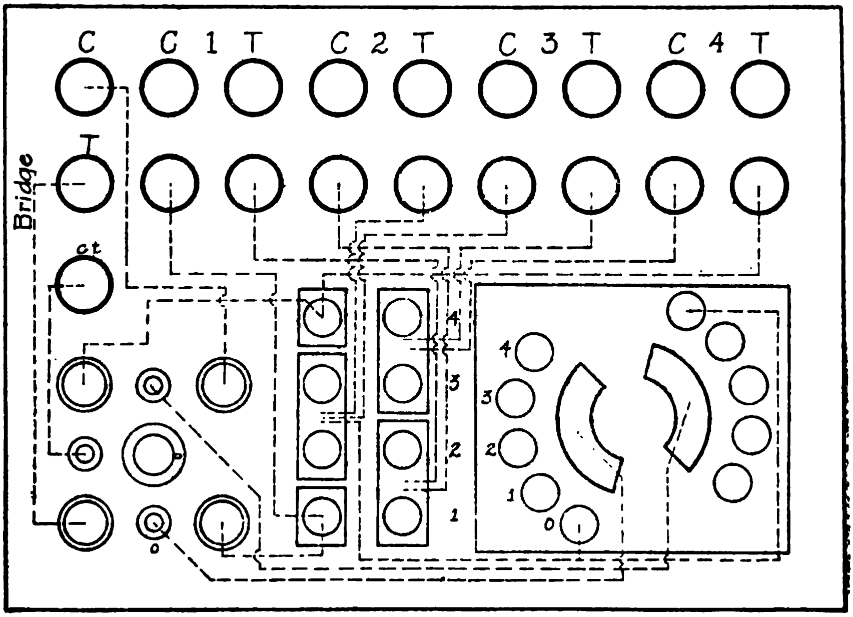
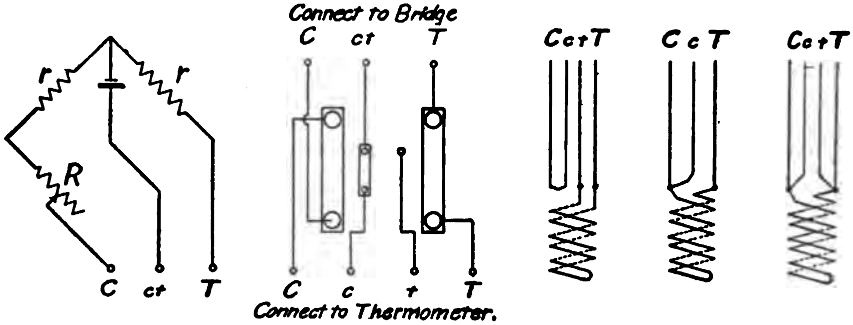


FIG. 9.—*Plan of commutator and interchanger for four thermometers.* (*Scale half size.*)

8. NOTATION

The notation used in this paper is applicable to either the Callendar compensated type of thermometers, the Siemens type, or the potential-terminal type. The terminals of the bridge, the commutators, and of the thermometers are marked as shown in Fig. 10.

It is obvious that the potential-terminal thermometer should not be connected directly to the bridge. The Callendar or Siemens type thermometers are connected directly to the bridge, connecting terminals with the same marking. Thermometers of these types may also be connected to the commutator and measured when the commutator is in the normal (N) position. If a thermometer of the Callendar type is connected to the commutator, both the *c* and *t* leads must be connected to the point *c* of the commutator. It is preferable to mark the two "C" leads of a Callendar thermometer alike and also the two "T" leads. If this is done the marking of the leads will serve to distinguish between a thermometer of the Callendar type and one of the potential terminal type.



Wheatstone Bridge **Commutator** **Callendar Thermometer** **Siemens Thermometer** **Potential Terminal Thermometer**

FIG. 10.—*Diagrams to illustrate notation*

A potential terminal thermometer may evidently be used in the Siemens bridge as a three-lead compensated thermometer and eight different combinations, of which four are independent, may be made with the four leads. It is often desirable to be able to use a thermometer either as a three-lead or as a potential terminal resistance. For example, in calorimetric measurements, the use of the commutator would prove inconvenient, and it is improbable that the accuracy attained could be increased in this way. To avoid ambiguities the resistance of the thermometer when used in the Siemens bridge is defined as the combination

$$X+T-C$$

This requires the use of the lead marked *c* as the third lead. If this thermometer is used with a commutator adjusted as previously described, the data obtained with the commutator in the normal (*N*) position will be applicable to the three-lead thermometer, while the complete data (commutator "*N*" and "*R*") will be applicable to the potential terminal thermometer, and a separate calibration of the three-lead thermometer is not necessary.

9. SUMMARY

A type of Wheatstone bridge suitable for use in resistance thermometry is described, in which plugs or dial switches are used and the circuits so arranged that the errors due to contact resistances are no greater than with the mercury contact bridges heretofore used. The application of these bridges to the measurement of resistances with potential terminals is described. A convenient interchanger by means of which several thermometers may be successively measured with one bridge is also described.

The methods described in this paper have been gradually developed to meet the demands of the Bureau's work in resistance thermometry and represent therefore the joint work of numerous members of the Bureau staff. A number of the arrangements used were suggested by Dr. Dickinson and Dr. Wenner of the Bureau.

WASHINGTON, May 20, 1916.

THE DAMPING OF WAVES AND OTHER DISTURBANCES IN MERCURY

By M. H. Stillman, Assistant Physicist

In connection with some work on the adjustment of mercury surfaces, done by the writer some time ago,[1] considerable difficulty was experienced by reason of the small waves that formed on the surface of the mercury as a result of the trembling of the support of the vessel containing the mercury. The present paper describes a method by which such disturbances of a mercury surface, as well as larger disturbances of the mercury as a whole, can be partially or wholly eliminated.

This method consists in subjecting the mercury to a strong magnetic field, the direction of the field being approximately at right angles to the direction of motion or of impending motion of some portion of the mercury. The motion of the mercury across the magnetic lines of force tends to produce an electric current, the reaction of which with the lines of force tends to stop the motion of the mercury.

Let l = the effective length of an element of mercury which is cutting the magnetic lines of force at right angles and the axis of which is at right angles to the lines of force.

v = the velocity of the element of mercury in a direction at right angles to the lines of force and to the element.

---

[1] Stillman, this Bulletin **10**, p. 371, Scientific Paper No. 214; 1913.

E = the electromotive force produced in the element by the motion of the mercury relative to the lines of force.

I = the electric current produced in the element by this electromotive force.

R = the electrical resistance of the elementary circuit.

ϕ = the number of lines of force linked with the elementary circuit.

B = the flux density; that is, the number of lines of force per unit area taken perpendicular to the direction of the lines of force.

f = the electromagnetic damping force on the element of mercury per unit length.

Now $f = IB$

$$I = \frac{E}{R} \text{ and } E = \frac{d\phi}{dt}$$

But $\dfrac{d\phi}{dt} = lvB$

So that $I = \dfrac{lvB}{R}$

$$\therefore f = \frac{lvB^2}{R}$$

A constant K is placed before the second member of this equation to indicate that the numerical value is dependent upon the units used. The equation is then written

$$f = K\frac{lvB^2}{R}$$

If f is expressed in dynes, l in centimeters, v in centimeters per second, B in gausses, and R in ohms, K will be 10^{-9}, so that

$$f = 10^{-9}\frac{lvB^2}{R}$$

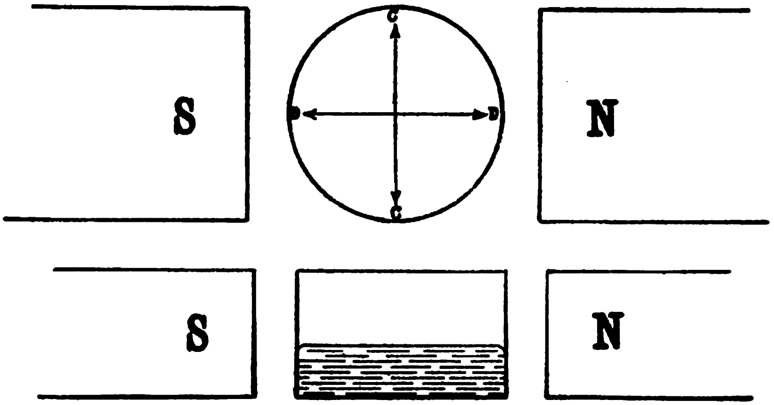
The total damping force, F, is then the sum of the damping forces on all of the elements; that is,

$$F = 10^{-9}\sum\frac{lvB^2}{R}$$

This clearly indicates the methods by which the damping can be varied.

In order to determine the effectiveness of the method, the experiments described below were performed. Mercury to a depth of about 1 cm was placed in a glass dish which had a diameter of 43 mm and this was then placed between the poles of an electromagnet, Fig. 1. The field of this magnet was horizontal and its intensity was varied between 2500 and 10 000 gausses during the experiments. It was found that if the mercury were violently agitated as a whole while outside of the magnetic field and then brought into the field, the motion was strongly damped. The magnitude of the damping in a field of given strength was, as expected, dependent upon the direction of motion of the mercury relative to the direction of the field. Thus, while violent oscillations of the mercury in the direction *CC* at right angles to the direction of the field persisted for a short time—although brought to rest much sooner than they were outside of the magnetic field—oscillations in the direction *DD*, parallel to the field, were damped out almost instantly. Keeping the mercury in the field, it was found to be very difficult to produce large oscillations in the direction parallel to *DD* when the field strength was no greater than approximately 7000 gausses.

Top view



Side view

Fig. 1.—*Diagram of arrangement of apparatus*

It is of some interest and importance to consider the conditions that are responsible for the differences in damping of the oscillations of the mercury in different directions. Fig. 2 represents the conditions existing when the horizontal oscillations of the mercury are at right angles to the lines of force of the field. Fig. 3 represents the corresponding conditions when the direction of the horizontal motion is parallel to the direction of the field.

Considering Fig. 2, when the horizontal motion of the mercury as a whole is in the direction shown by the double arrows, an upward-directed emf is developed in accordance with the laws of electromagnetic induction in all parts of the mercury so moving; but inasmuch as there is no adequate return circuit available, very little current flows and therefore, in accordance with the formula, there is very little damping. In addition to this hori-

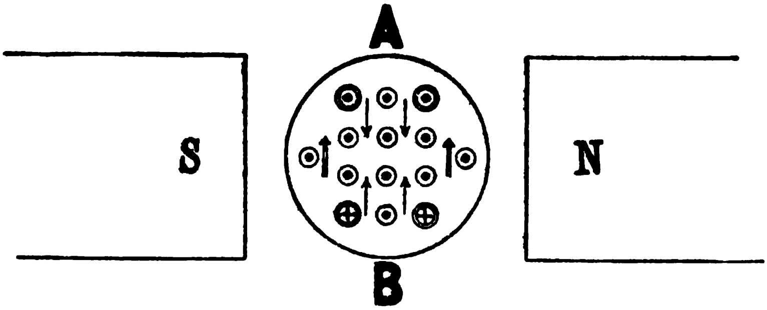
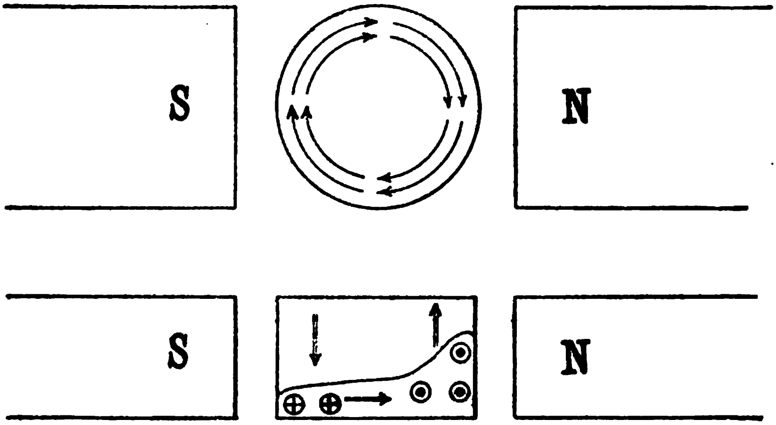


FIG. 2.—*Horizontal motion of mercury at right angles to lines of magnetic force*

Top view



Side view

FIG. 3.—*Horizontal motion of mercury in direction of lines of magnetic force*

Legend for figures 2 and 3

⟹ Direction of motion of the mercury

⟶ Direction of induced emf or current

● Mercury rising

⊕ Mercury falling

◉ Induced emf or current directed upward or toward observer

⊕ Induced emf or current directed downward from observer zontal motion of the mercury, there is a vertical upward motion at the far side (*A*) of the vessel and a corresponding downward motion at the near side (*B*). This produces two opposing emf's, as illustrated in Fig. 2, so that also by this last-mentioned type of motion little current is produced and consequently the damping is small.

In Fig. 3, which illustrates the conditions existing when the horizontal motion of the mercury is parallel to the lines of force of the field, it is evident that no emf and therefore no current is produced by this horizontal motion. But, as in the type of motion first considered, this horizontal motion is accompanied by a rising of the mercury on one side of the vessel and a corresponding falling on the other side. These movements in opposite directions produce emf's in opposite directions, but instead of opposing, these reinforce each other and hence produce a current as illustrated in the figure.

The fact brought out in the above discussion, namely, that an electric current of an effective magnitude in the mercury is often prevented by opposing electromotive forces or lack of a return circuit of low resistance, suggested that if the containing vessel were of some nonmagnetic metal of low resistance instead of the electrically nonconducting glass, and if the mercury were in good electrical contact with the metal, much greater damping might be expected to occur, especially of those oscillations which involve a horizontal movement of the mercury across the lines of force. Accordingly, a brass vessel was constructed, its interior having the same dimensions as that of the glass vessel and having walls about 5 mm thick. This was supplied with the same quantity of mercury as that contained by the glass vessel and then the oscillations of the mercury in the two vessels were compared, both inside and outside of the magnetic field. As was to be expected, the motion of the mercury in the two vessels when the magnetic field was not present was practically the same. When, however, the magnetic field was present the effectiveness of the metallic container in comparison with the glass container in aiding the magnetic damping of the mercury was very marked. This advantage was especially evident when the horizontal motion of the mercury was perpendicular to the direction of the magnetic field, the time taken to completely damp the oscillations being only a small fraction of that required when the glass vessel was employed.

For continued use a plain brass vessel would of course not be satisfactory because of the tendency of brass and mercury to amalgamate. A nickel-plated copper or brass vessel would probably be very successful, combining resistance to amalgamation with low electrical resistance. When a glass containing vessel must be used, a nonmagnetic wire netting of low electrical resistance and not easily amalgamated might be submerged just below the surface of the mercury. This would aid the magnetic field in damping the oscillations by providing the induced electric currents with a return path of high conductivity, and it would also tend to damp these oscillations mechanically.

These above-described experiments refer to the damping out of the relatively large oscillations or other large disturbances in a mass of mercury, and it is this type of disturbance that the method is particularly effective in reducing or obviating, since the damping is directly proportional to the velocity of the mercury. However, the writer has also found that the smaller ripples on the mercury surface may also be strongly damped by the use of the magnetic field. In these experiments it was found that even by the use of the parallel transverse magnetic field used in the previously described experiments—a type of field not especially well adapted to this purpose—the ripples were damped out in less than one-half of the time required for them to subside unaided. By carefully designing the mercury container and the magnetic field, making use of the facts expressed in the equation, the damping of these waves could be much increased.

Attention should be called to the fact that it is not always necessary to expose the entire surface of the mercury to the magnetic field in order to secure this damping effect on the ripples; but, since the damping force varies as the square of the field strength, it would in many instances be more economical to make the field strength large and to limit its operation to a comparatively small area at that portion of the system where the mercury motion and the electrical conductivity are most favorable for damping.

While, as it is almost unnecessary to state, some simpler method than above described may generally be used to damp out the motion in a mass of mercury, it is very probable that this method used by itself or in conjunction with some other method will frequently be found to have distinct advantages. It is suggested that it might sometimes be used when accurate adjustments of mercury surfaces at sea are desired and in other places where unsteadiness of the mercury container is unavoidable.

WASHINGTON, April 15, 1916.

A VARIABLE SELF AND MUTUAL INDUCTOR

By H. B. Brooks and F. C. Weaver

CONTENTS

Page
1. Necessity for developing the instrument 569
2. Existing instruments and their limitations 570
3. Preliminary basis for the design 571
4. Scale law of circular coils 572
5. Scale law of link-shaped coils 572
6. Description of the new instrument 576
7. Design procedure 578
8. Other instruments of similar form 579
9. Desirable features in a variable inductor 580

1. NECESSITY FOR DEVELOPING THE INSTRUMENT

In the work of testing current transformers at this Bureau the need arose for a variable inductor,[1] to have a range of variation of about 1 millihenry and to carry 5 amperes continuously. It was also necessary that the resistance should be as low as practicable consistent with reasonable dimensions. As no instrument meeting the requirements was on the market, the design of an apparatus of this kind was undertaken.

The type of instrument which was devised as a result of this investigation is not limited in its application to the work of testing current transformers, but is applicable wherever it is necessary to vary the self-inductance of a circuit or the mutual inductance between two circuits while keeping the resistance constant. It was therefore considered desirable to give a description of the apparatus and to compare its performance with that of other instruments now available for this class of work.

---

[1] The expression "variable inductor" is suggested for such instruments as being preferable to the usual wordings "variable inductance," "variable standard of inductance," or "variable standard of self-induction." It is felt that the word "inductance" should be reserved for the property of the apparatus and should not be used for the apparatus itself. A similar tendency is seen in the growing use of the word "resistor" to signify a coil, grid, or other device used because of its resistance.

2. EXISTING INSTRUMENTS AND THEIR LIMITATIONS

The first commercial variable inductor was the one designed by Ayrton and Perry,[2] in which the fixed coil and the moving coil are each wound as belts on concentric spherical surfaces. While this inductor would give the required values of resistance and inductance if wound with wire of suitable size, it has the drawback of being non-astatic. The coils inclose a large area, and when current flows through them a very appreciable magnetic field is set up which may affect other parts of the circuit. Conversely, the variation of magnetic fields set up by other parts of the circuit will induce disturbing electromotive forces in the coils. In either case errors of appreciable amount may arise unless care is taken to keep individual instruments at a sufficient distance apart.

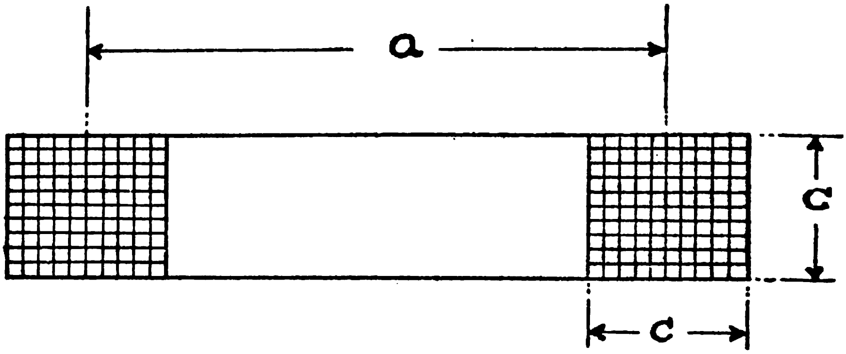


Fig. 1.—*Coil of Maxwell proportions for maximum time constant*

Two other commercial forms were available, namely, the Mansbridge,[3] and a form similar to it in external appearance, originally made by Nalder Bros. & Co. Each of these instruments consisted of two circular plates of hard rubber, the lower plate containing two fixed coils, while the upper plate, containing two similar coils, could be turned about a central pivot carried by the lower plate. The scale divisions of the Nalder instrument were very unequally spaced, and the time constant of the Mansbridge instrument, in the size in which it is regularly manufactured, was too low for the given special purpose.

---

[2] Electrician (London), 34, p. 546; 1895.

[3] United States Patent No. 893340, issued July 14, 1908, to G. F. Mansbridge.

3. PRELIMINARY BASIS FOR THE DESIGN

As a starting point in the new design, use was made of the proportions given by Maxwell[4] for a circular coil of square cross section to give the maximum value of time constant for a given mass of wire. Such a coil is shown to scale in Fig. 1. Maxwell stated that for maximum time constant the mean diameter a should equal 3.7 times the side c of the winding cross section.[5] The original idea was to use two sets of interleaved[6] coils, each set when in the position of maximum inductance to be equivalent to a single coil of the Maxwell proportions. The arrangement is shown diagrammatically in Fig. 2, where F_1 and F_2 are the fixed coils of the left-hand group and M_1 the moving coil. By making M_1 of twice the axial thickness of either fixed coil, so that it contained as many turns as F_1 and F_2 together, the inductance of the group with M_1 opposing the fixed coils has as low a value as can be obtained, except by subdivision of the group into five, seven, nine, etc., sections. While this further subdivision is possible, it was thought best for mechanical considerations to limit the number of coils in each group to three.

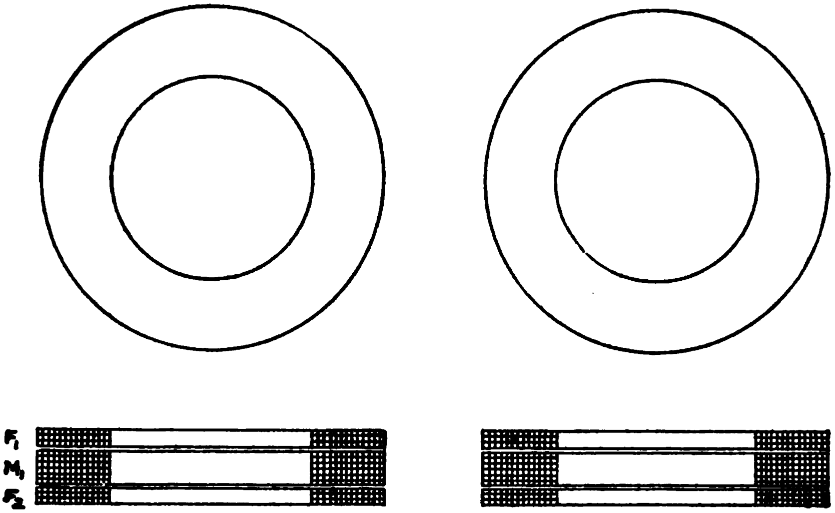


FIG. 2.—*Sets of interleaved coils as used in experimental variable inductor*

---

[4] Maxwell, Electricity and Magnetism, 3d ed., 2, pp. 345–346.

[5] It has recently been shown that for maximum time constant the mean diameter a should be three times the side c. See paper by Shawcross and Wells, Electrician, 75, p. 64; 1915.

[6] This interleaving of the coils was felt from the start to be an important feature for reasons given on p 579 in the discussion of the Nalder and the Mansbridge inductors.

4. SCALE LAW OF CIRCULAR COILS

As there was reason to fear that the scale law of such a variable inductor might not be satisfactory, a wooden frame carrying two such sets of coils was constructed to test this point experimentally, since to do so by mathematical analysis would be very difficult.[7] The apparatus is shown in Fig. 3 and the curve *A* in Fig. 4 shows the manner of variation of the inductance when the moving coils are turned through 180°. It will be seen that at two angular positions the rate of change of the inductance is zero, and hence in the vicinity of these points no scale divisions can be placed. Also, between the positions 75° and 110° the inductance decreases with increasing angle, while over the rest of the range the reverse is true. The scale of such an instrument would therefore not be figured between, say, 60° and 120°, and its use would be very inconvenient, especially when making settings in balance methods without looking at the scale.

Experiments were made with the two groups of circular coils at different distances apart. It was found that when the two groups were brought almost into contact a much better scale law was obtained. However, such an arrangement leaves no room for the shaft about which the coils must rotate, and further improvement was sought by modifying the form of the coils.

5. SCALE LAW OF LINK-SHAPED COILS

It was very desirable to secure a uniform scale, while keeping each group of coils as close to the Maxwell proportions as possible. By empirical reasoning the cause of the unfavorable part of curve *A*, Fig. 4, was ascertained, and the conclusion was reached that the defect might be eliminated by elongating the coils into an approximately elliptical form with the longer axes perpendicular to the line joining the centers of the two coil groups. Trial with a rough model gave encouraging results. The new curve did not show the undesirable maximum and minimum of curve *A*. The inductance increased continually as the moving coil was turned from the initial position, but the curve was such as to give scale divisions of very unequal length in different parts of the range.

A large number of experiments were now made, in which the form of the coil, the spacing of the coil groups, and the angle

---

[7] A. Campbell, Phil. Mag., 6th series, **15**, p. 167; 1908. S. Butterworth, Phil. Mag., 6th series, **31**, p. 443; 1916.

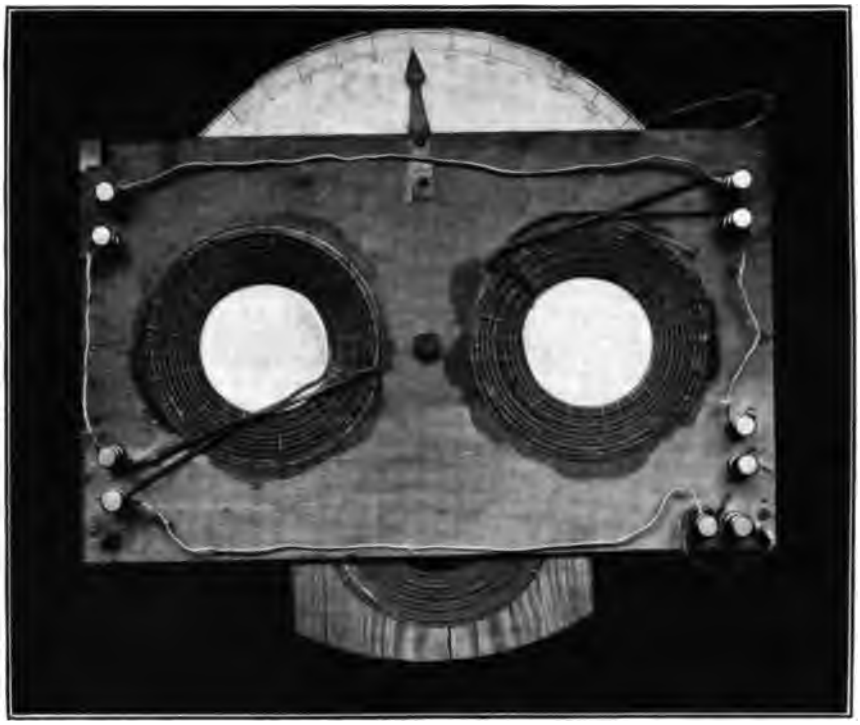


FIG. 3.—*Experimental variable inductor with circular coils*

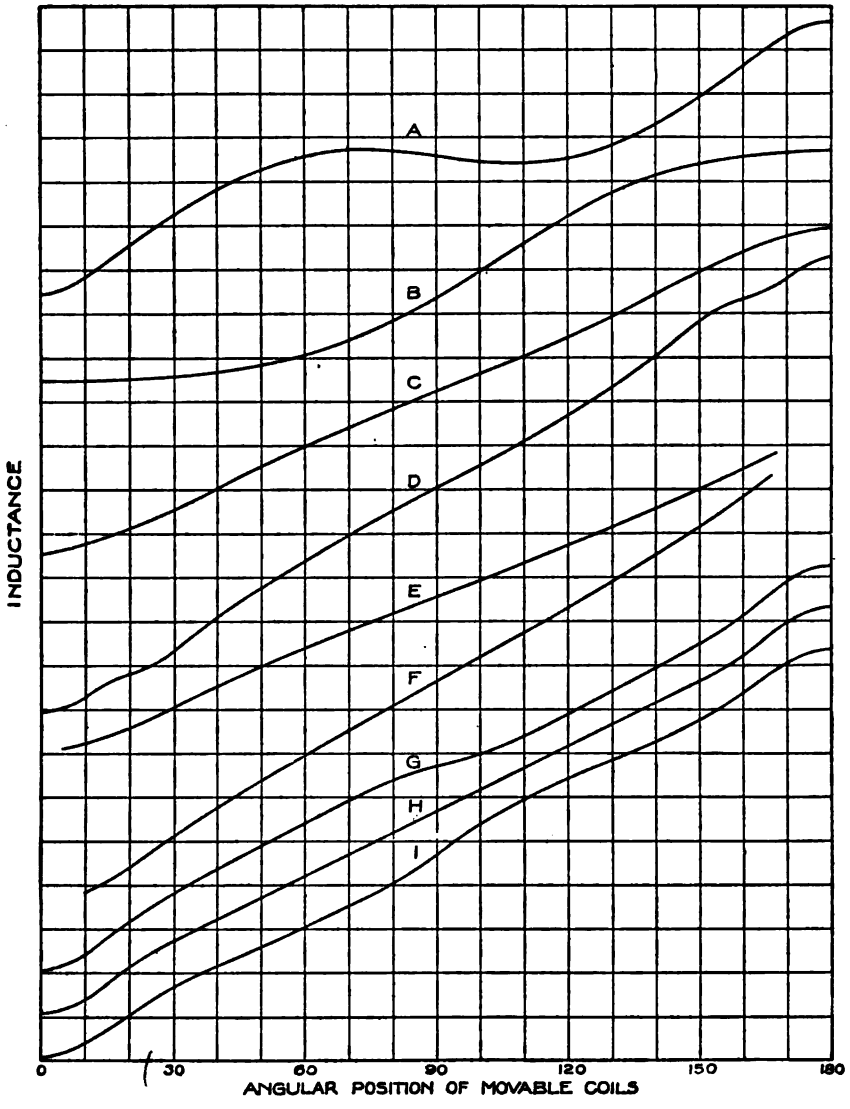


FIG. 4.—*Curves showing manner of variation of inductance of several forms of variable inductor*

between the longer axes of the coil and the line joining the centers of the coil groups were each varied separately, a curve being determined for each case. While several arrangements were found which would give scales as uniform as those of other variable inductors in use, the advantages[8] of a linear scale (one having divisions of uniform length) are so great that the work was continued until a compact arrangement of coils of simple geometric form and high time constant was determined which gave this result, as closely as physical limitations seem to permit. In the course of this work valuable suggestions were received from Dr. F. W. Grover and Dr. H. L. Curtis.

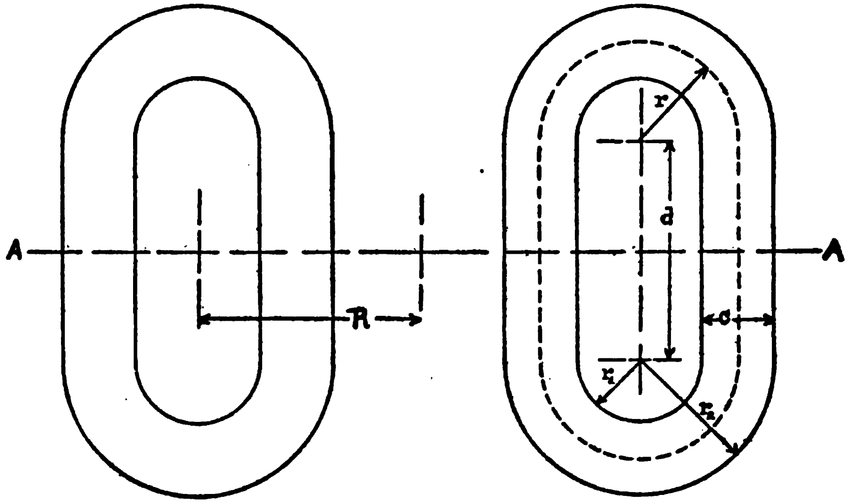


FIG. 5.—*Plan of link-shaped groups of coils*

The arrangement is shown in plan in Fig. 5. The link-shaped coil groups may be thought of as made by cutting the circular coil groups in halves by a plane at right angles to the plane of the coils, separating the two halves by a distance *d*, and then joining the cut surfaces by straight portions of winding to complete the link. The depth of the group, perpendicular to the paper, equals *c*, the radial breadth. The centers of the two coil groups are separated by a distance 2*R*. To secure uniformity of the scale requires a particular value of *R*, the half distance between the centers of the coil groups. The relative values were determined to be as follows, r being the mean radius of the circular part of the coil.

---

[8] These advantages are, in part, as follows: The scale is easier to make and it is easier to interpolate between divisions. In checking the instrument from time to time, fewer points need to be tested. If a small displacement of the scale or of the fiducial mark occurs, a small error is introduced which is of nearly the same absolute value for all points of the scale, while for an instrument having scale divisions of very unequal length the same displacement may make the absolute error in some parts of the scale much greater than in others.

$$c=0.78r$$
$$d=2.2r$$
$$R=2.26r$$

From these relations it follows that—

$$r_1=0.61r$$
$$r_2=1.39r$$

Referring to Fig. 4, the three curves *G*, *H*, and *I* show the effect of a variation of dimension *R* on the scale law. Curve *H* is for the normal value of *R* (=2.26*r*) and gives a linear scale over the angular range of 30° to 150° movement from the initial position. The curve must become horizontal at 0° and 180°, and it will be noted that the change of slope from 30° to 0° and 150° to 180° is gradual. Curve *G* shows the effect of increasing *R* by 6 per cent. Since the length of a scale division at any part of the curve is proportional to the reciprocal of the slope of the curve, the divisions would be about twice as large at the 90° position as over the range from 30° to 70° or from 110° to 150°. A similar condition exists in curve *I*, for which *R* was 6 per cent smaller than normal value, but in this case the scale divisions are about three-fourths as long at 90° as in the other two parts of the scale above mentioned.

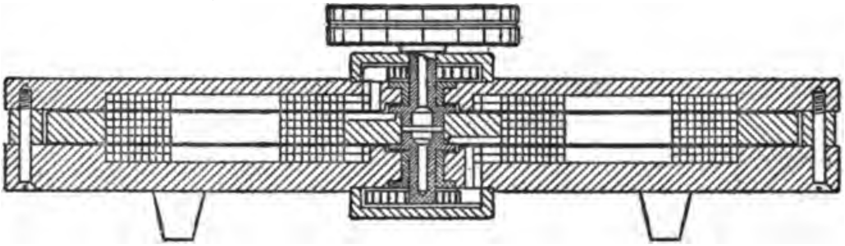


FIG. 6.—*Cross-sectional view of variable inductor*

Curves *B* to *F* of Fig. 4 are given for comparison. *B* is for a Campbell mutual inductor,[9] and was determined from measurements of the scale of the instrument. *E* and *F* are for the lower and higher ranges of a Mansbridge variable inductor, and were plotted from a facsimile scale given in a circular issued by the (American) maker. Curves *C* and *D* are for variable inductors of Ayrton-Perry form, made by an American firm.

---

[9] A Campbell, Phil. Mag., 6th series, 15, pp. 155–171; 1908. In this instrument the difficulty shown by curve *A* is avoided by using a circular moving coil eccentrically pivoted between two fixed circular coils which are at a relatively large distance apart. This arrangement, however, is not suitable for use as a variable self inductor, because it makes the mutual inductance so small in comparison with the self inductance. This would result in a very small ratio of maximum inductance to minimum inductance.

6. DESCRIPTION OF THE NEW INSTRUMENT

Using the proportions given on page 575, a variable inductor was constructed by Joseph Ludewig, of the instrument shop of this Bureau. Fig. 6 shows a cross section along the line *AA* of Fig. 5. The value of r, the mean radius of the circular part of the coils, is 36.8 mm. The coils are mounted in three hard-rubber disks, of which the inner one is provided with bronze spindles which turn in brass bushings in the upper and lower plates respectively. The two outer disks are held together by six screws and separating pieces and form the body of the instrument. The diameter of these disks is 35.5 cm (14 inches). The bronze spindles of the movable disk also serve to carry current to and from the moving coil. Heavy copper spirals protected by hard-rubber caps carry the current to the spindles. It was not considered feasible to carry current through the bearing, as a variable and uncertain resistance is very bad in the secondary circuit of a current transformer and makes serious trouble in most work for which a variable inductor is used. Stops are provided to limit the motion of the inner coil to 180°.

The actual number of turns of wire is shown in Fig. 6. For example, each fixed coil is wound in nine layers of two turns each. The wire is stranded, being made of seven insulated copper wires of 0.8 mm. diameter (No. 20 B. & S. gage), the conductor so formed having a cross-sectional area of 3.6 mm^2. The design was made on the basis of a range of variation of 1.1 millihenrys. The uniformity of the scale may be seen from Fig. 7, which shows the inner disk alone. The scale is figured in microhenrys, each division being 5 microhenrys. The useful part of the scale is from 125 to 1225 microhenrys. From 325 to 1025 microhenrys the scale is uniformly divided to within the limits of the measurement of the inductance. It is not possible to secure an arrangement of coils which will give a uniform scale through the entire 180°, as this requires either that the fixed coils and the movable coils would have to coincide at 0° and 180° or each coil group would have to contain an infinite number of infinitely thin sections.

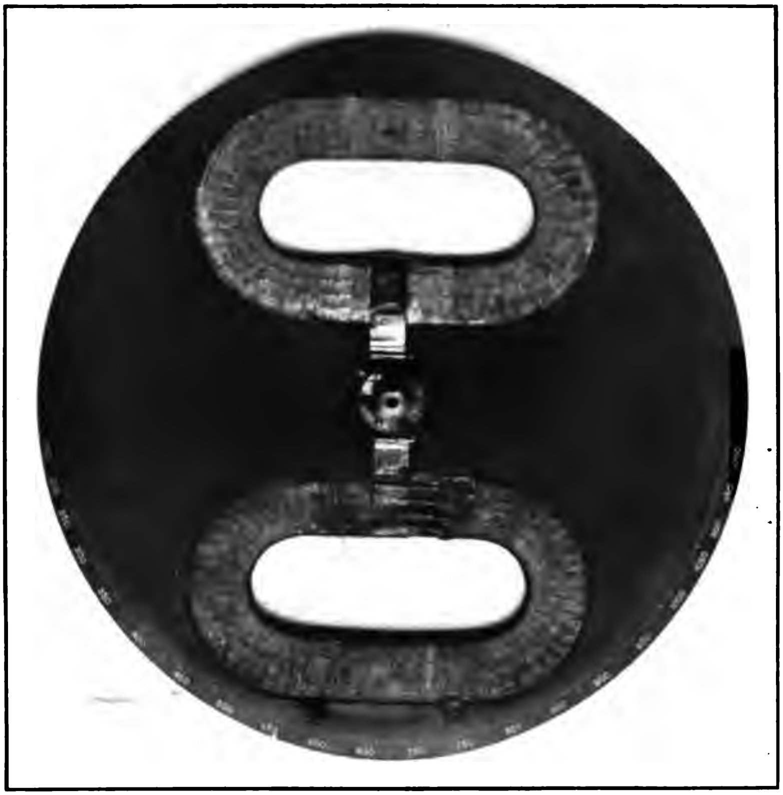


FIG. 7.—*Inner disk of variable inductor, about ¼ size*

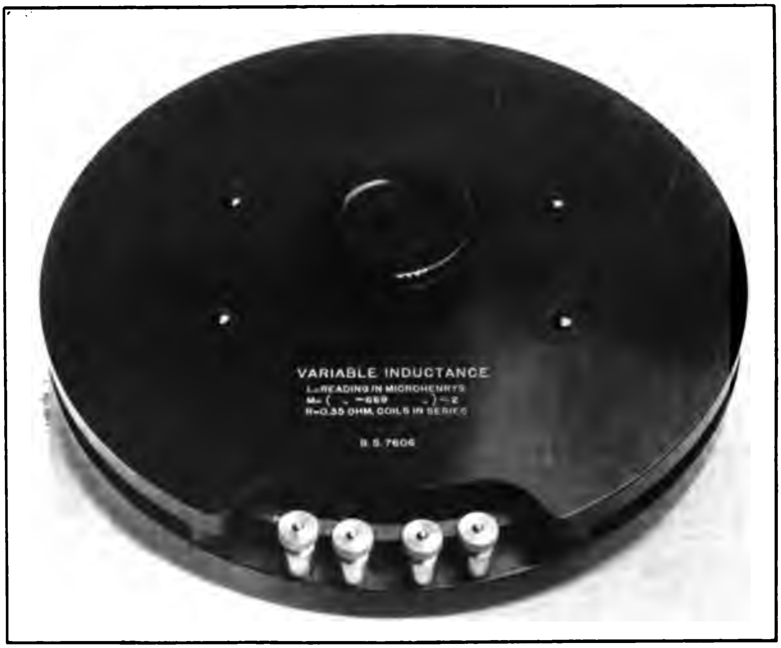


FIG. 8.—*Variable inductor, about ¼ size*

However, it will be noticed that below 325 and above 1025 microhenrys the length of the scale divisions decreases gradually until the points 150 and 1175 are reached. There are no points within the working range where abrupt change of scale law occurs, and this fact assists greatly in making an accurate scale and in interpolating between adjacent scale divisions.

The four fixed coils are connected in series and brought out to two binding posts, and the two movable coils in series to another pair of binding posts. The scale is figured to read the self-inductance with all the coils in series. By using the fixed coils and the movable coils as primary and secondary the instrument becomes a variable mutual inductor. To avoid confusion, a scale for reading the values of mutual inductance was not added. The mutual inductance is found[10] by subtracting 669 microhenrys from the reading and dividing the remainder by 2. A table of values of mutual inductance corresponding to readings on the self-inductance scale may be used.

With the coils in series the resistance is 0.35 ohm and the time constant for maximum inductance setting is 3.4 milliseconds.[11] The time constant of the Ayrton-Perry inductor, which occupies several times the space required by the form herein described, is about 4.5 milliseconds, and that of the Mansbridge is 1.6 milliseconds. In comparing time constants of different types of inductors, it should be remembered that a fair comparison must take into account the relative space occupied by each instrument. The time constant for any model may be increased by increasing the dimensions.

The complete instrument is shown in Fig. 8. The upper fixed disk is cut away to show the scale and has a fiducial mark. The instrument has been in use for several years and has been satisfactory except that trouble has occurred at times from the sticking of the moving disk. At the time the instrument was planned hard rubber was known to be liable to gradual change of form,

---

[10] In any such arrangement of two sets of coils whose mutual inductance can be varied by change of relative position,

$$L = L_1 + L_2 \pm 2M_{12}$$

where L is the total self-inductance, L_1 is the self-inductance of one set of coils alone, L_2 that of the other, and M_{12} the mutual inductance of one set on the other. When the coils are so placed that M_{12} is zero, $L = L_1 + L_2 = C$, a constant for the given apparatus. From this it follows that for any position of the coils

$$\pm M_{12} = \frac{L-C}{2}$$

[11] This value would be greater if solid wire were used, as would be the case for smaller wire for ordinary frequencies, because the space factor of the stranded conductor is low. The conductor being rather large, it was thought best to strand it as a precaution against change of inductance with frequency.

but it seemed to be the best material for the purpose when making a single instrument by machining the disks to shape. The use of modern molded insulating materials gives promise of satisfactory performance in this respect. Referring to Fig. 6, the connections are such that the two sets of fixed coils have opposite magnetic polarities, as viewed from above, and the two moving coils also have opposite polarities. This astatic construction tends to reduce trouble from stray magnetic fields.

7. DESIGN PROCEDURE

In the design of the windings to give a definite maximum inductance the general procedure was as follows. The effect of mutual inductance between the left-hand group of coils (Fig. 6) and the right-hand group contributes 3 per cent to the total self-inductance of all the coils in the position for maximum inductance, but this may be neglected and each group be computed to give one-half of the maximum value of self-inductance required. Each group is considered as a coil of square cross section which may be imagined as having been originally wound as a circular coil and then flattened into the link form. For design purposes, where an accuracy of 1 or 2 per cent suffices, it may be stated that the inductance of the link-shaped coil will bear the same ratio to the inductance of the circular coil as the area inclosed by the mean turn of the link-shaped coil bears to the area inclosed by the mean turn of the circular coil.[12] The inductance of the circular coil is conveniently calculated with sufficient accuracy by Maxwell's approximate formula.[13]

However, a simpler design procedure may now be based on the observed performance of the instrument here described, and from its constants new values of dimensions and of number of turns of wire may be computed to meet any given requirements. First, the time constant may require to be changed. This may be accomplished by changing all the dimensions, while keeping the same proportions. The factor m, by which all the dimensions must be multiplied, may be found from the relation that for coils of similar form wound with wire having the same space factor the time constant varies directly as the square of a given linear dimension and is independent of the size of the wire. The inductance, however, varies as the first power of a given dimension, hence the inductance of the new set of coils will be m times the inductance of the original set.[14] This value of inductance will not be what is wanted, in general, and the size of the wire to be used[15] to give the desired inductance may be found from the relation that for a coil occupying a given space the inductance varies directly as the square of the number of turns of wire in the coil.

---

[12] This ratio for the instrument here described is 0.830.

[13] Maxwell, Electricity and Magnetism, 3d ed., 2, pp. 345–346.

It is a good plan to check the computed results by making a temporary wooden form in which can be wound a trial coil of the computed size of wire occupying the same space as the three coils composing one-half the windings of the instrument; that is, two fixed coils with the moving coil between them. This coil should have an inductance equal to one-half of the maximum value of inductance desired in the finished instrument at the upper end of the range.

8. OTHER INSTRUMENTS OF SIMILAR FORM

This instrument was designed and constructed about five years ago. Since then a number of similar ones have come to our notice. One designed by Rendahl[16] and made by the Gesellschaft für drahtlose Telegraphie has two D-shaped coils in a circular hard-rubber plate above which turns a similar plate and set of coils. The coils were wound in sections so that the range may be varied by changing the connections. Very similar instruments were patented by Ferrié and by Einstein.[17] We have no information concerning the scale law of these instruments or the relative dimensions of their parts. They have an inherent defect which is also found in the Nalder[18] and Mansbridge forms, namely, that a slight axial displacement of the disks from their normal relative position will appreciably change the inductance. Such a displacement may result from wear or loosening of the bearing, or from change of form of the disk.[19] In the construction described in this paper, the disks holding the two sets of fixed coils are rigidly connected. A slight axial displacement of the movable disk will not affect the inductance, because the change caused by its movement away from one fixed disk is compensated by the change caused by its approach toward the other.

---

[14] This assumes that the number of turns of wire is not altered. If all the dimensions of a coil are increased to m times their original value, the size of the wire remaining unchanged, the inductance increases to m^5 times its original value.

[15] The wire must of course be large enough to carry the desired current.

[16] Markau, Die Telephonie ohne Draht, pp. 96–98; 1912.

[17] Nesper, Jahrbuch der drahtlosen Teleg. und Teleph., 2; pp. 326–339; 1908–9.

[18] The variable inductor referred to in this paper as the Nalder is no longer made by Nalder Bros. & Co.

[19] Hard rubber (ebonite) yields slowly to stress, behaving somewhat like a very viscous liquid. Its high electrical resistance and the ease with which it can be machined have caused it to be very widely used in spite of its defects. It has the drawback of suffering great depreciation of its surface insulation when exposed to light, moisture, and dust.

9. DESIRABLE FEATURES IN A VARIABLE INDUCTOR

The desirable features to be obtained in a variable inductor are given below, on the assumption that the instrument is used to give variable self-inductance.

1. High time constant (ratio of inductance to resistance) for the space occupied by the instrument. This should be based on the maximum value of the inductance at the upper end of the useful part of the scale and not on any greater value which is beyond the useful part of the scale.
2. Large ratio of the maximum inductance to the minimum inductance. Neither of these values must be outside the useful part of the scale.
3. Astaticism.
4. Linear scale.

It is probable that the instrument herein described fulfills requirements 1 and 4 about as well as can be done. Some gain in time constant may be possible by starting with coils having Maxwell proportions as corrected by Shawcross and Wells,[20] since this would give a slightly more compact coil as the starting point. The improvement may not be great enough to warrant the labor of determining by trial the relative dimensions for uniform scale, though if such a scale is possible, the labor would doubtless be much less than that required in determining the proportions given in this paper.

Requirement 2 can be more fully met, though at some sacrifice of 1, by reducing the axial thickness of the coil. Experiments were made with coils of one-half the thickness given by the proportions of page 575. It appeared to be feasible to increase the ratio of maximum to minimum to about 18 or 20, but this gain is offset by a loss of about 40 per cent in the time constant.

Requirement 3 could be more fully met by a design using four sets of coils spaced 90° apart around the circular disks, but this would reduce the scale to one-half its present length.

It is therefore believed that the present design most nearly balances conflicting requirements, and that the labor of developing the other forms would only be justified if unusual requirements were to be met.

WASHINGTON, May 26, 1916.

---

[20] Shawcross and Wells, Electrician, 75, p. 64; 1915.

A SYSTEM OF REMOTE CONTROL FOR AN ELECTRIC TESTING LABORATORY

By P. G. Agnew, W. H. Stannard, and J. L. Fearing

CONTENTS

Page
I. Introduction 581
  1. Scope 582
II. Choice of System 582
  1. Advantages of using a single rheostat 582
  2. Methods available 583
  3. Reasons for choice 583
III. Field Rheostats 585
  1. Insulation 586
  2. Winding 586
  3. Brushes, etc 586
  4. Mounting of tubes 586
  5. Cooling system 587
  6. Design of windings 587
IV. Rheostats for Control of Direct Current and Voltage 590
  1. Voltage rheostats 590
  2. Current rheostats 590
V. Phase Control 592
VI. Operating Details 592
  1. Motors 592
  2. Power for operation 592
  3. Controllers 592
  4. Jacks 593
  5. Automatic stop switch 594
  6. Wiring 595
  7. Motor fields 595
VII. Experience with System 596

I. INTRODUCTION

The remote control of electrical apparatus and machinery has an extensive technical application, but the range and precision of adjustment required in a great deal of laboratory work are greater than are provided for in regular commercial equipment. The apparatus here described is in use in the laboratory of the Bureau of Standards for testing electrical measuring instruments, instrument transformers, and similar testing and investigational work. Much of it would also be applicable to other purposes.

1. *Scope.*—The range and scope of a remote control system required for such work is well illustrated in testing wattmeters or watthour meters on low power factor, using separate sources for current and voltage. For the best conditions the observer should have both a coarse and a fine control of frequency, current, voltage, and power factor. If a test of the standard instrument on direct current is included, two other controls are necessary for the direct current and voltage. To accomplish this without the use of some system of remote control would require the observer to have access to at least 10 rheostats, 5 for fine and 5 for coarse adjustment, as well as to some phase shifting device.

As will be shown in detail later, the system described provides the same flexibility of control by the use of a single multiple-lever controller, each lever giving a two-direction, two-speed control of voltage, frequency, power factor, and current, respectively. The purpose of the two speeds is to provide coarse and fine adjustment. The controllers may be used in connection with any one of five motor-generator sets, each of which has three or more machines on the same shaft. Provision has been made to extend the system so as to include additional machines. The machines are all small, the largest having a capacity of but 25 kilowatts.

II. CHOICE OF SYSTEM

There are various arrangements which might be used for such a system of remote control, and it may be well to mention a few of the considerations which led to the adoption of the system described.

Most of the disadvantages which are mentioned below as applying to the various possible arrangements could be overcome by sufficient complication in design, but such detailed considerations can not be entered into here. Only a general outline of the simpler of the possible arrangements will be attempted

1. *Advantages of Using a Single Rheostat.*—Where both a wide range and fine steps are required it is customary to use two rheostats, one for fine and one for coarse adjustment. While this gives a wide range and accuracy of adjustment with relatively small rheostats, the wiring is considerably more complicated than in the case of a single rheostat, and two operating motors are required. Moreover, a single rheostat is more convenient to operate if it can be arranged to give the necessary range and accuracy of adjustment with a single control handle, as the annoyance of having to

continually change from one handle to another is obviated. In using two rheostats one frequently finds that he has reached the limit of the fine adjustment, and so has to change to the coarse adjustment and back again. From these and other considerations it was decided to attempt the use of a single rheostat with a single control handle, rather than one rheostat for coarse and one for fine adjustment.

2. *Methods Available.*—For the accuracy of adjustment and range of resistance required in the present case any ordinary slide-wire device, such as straight bifilar wires, or wires on the edge of a disk, was entirely out of the question. However, four different methods suggest themselves for securing the necessary range of resistance in a single rheostat suitable for motor operation. In each, coarse and fine adjustment may readily be secured by operating the motor at widely different speeds.

(*a*) Winding resistance wire (or tape) on a long, insulated tube, contact being made by a brush moved lengthwise on the tube, similar to well-known types of commercial rheostats. For short rheostats the brush may be driven by a worm, but for long ones it is practically necessary to operate it by a cord passing over a pulley driven by the motor. This is the method finally adopted. (For cross section of rheostat, see Fig. 1.)

(*b*) Tape or wire wound helically on the surface of a cylinder, the arrangement being such that the brush can make contact with any portion of the entire length of the wire or tape. Either the brush or the cylinder may be rotated, the other being stationary.

(*c*) Tape or wire wound from one reel to another. Contact may be made by special brushes, or the resistance may be short-circuited as it is wound on the metal reel, as is done in the Kelvin type of rheostat.

(*d*) A tape or wire arranged in the form of a flat spiral, the contact brush being moved along the conductor by a rotating arm. Provision would have to be made for motion of the brush radially in and out on the arm.

3. *Reasons for Choice.*—The first method was chosen because it is less complicated both in design and construction and generally better adapted to the ranges of current and resistance required for this particular installation than either of the other methods (resistance range, 0 to 1060 ohms; current range, 0.1 to 17 amperes). Self-cooling is more effective and artificial cooling more easily carried out than in either of the other methods. The con-

tact is distributed over several turns of conductor instead of being made on one conductor only. In cases in which a tapered rheostat is required the change from one size of wire to another, or from wire of one kind of alloy to that of another, is much more easily carried out in this method, without danger of trouble with the moving contact at the point of junction.

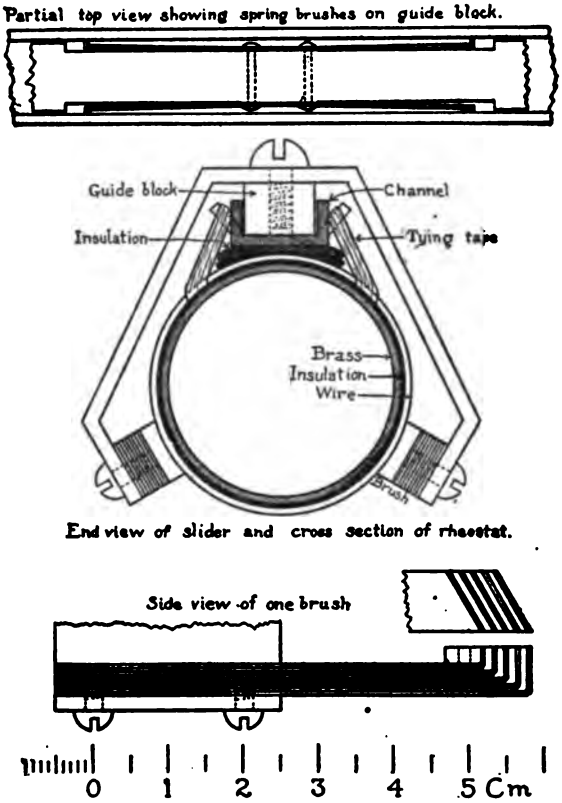
For compactness, tape would naturally be used in the third method, but in this case some mechanical complication would be necessary, as the two reels could not be directly geared together on account of the changing diameter of the reels as the tape is wound on and off. There would also be a danger of the conductor's breaking, either in regular use or in becoming accidentally fouled.

The fourth method was out of the question in the present case, since to keep the size within bounds the conductor would have to be too thin to withstand the mechanical strains. A minor objection is the changing curvature of the surface on which contact is made. A greater length of conductor is also necessary than in the other methods. This arises from the fact that the accuracy of setting depends upon the angular backlash, and since the outer turns are longer than inner ones, the length of conductor involved in taking up a given angular backlash is not a constant, but is proportional to the radius. Hence, for any predetermined law of accuracy of setting, a greater length of conductor is required than would be necessary if all the turns were of the same radius.

For larger currents, or lower voltage circuits, the second method would probably be preferable, as the first method does not lend itself as readily to the use of larger conductors, especially when accuracy of setting is of importance.

The method chosen (*a*) is, of course, not without its difficulties. The great length required for fine setting (up to 12 m in the present case) makes it inconvenient and somewhat unwieldy. Yet, where a group of rheostats is to be installed, the total space required is at most no greater than for the other methods. If a cord is used to move the brush, the stretching of the cord introduces lost motion, while if a steel tape is used there is danger of the windings being destroyed by short circuits in case of an accidental breaking of the tape. Theoretically, the method is at a disadvantage, since the adjustment is step by step, being limited to a turn of wire (or at best to a part of a turn), while in the other methods the adjustment is continuous. Practically, however, this disadvantage is largely only apparent, since the fineness of adjustment in the other methods is limited by lost motion, etc.

While the great length required in the rheostat makes the method seem a somewhat brutal solution of the problem, it forms a very simple, straightforward arrangement. Over two years' experience with it has been so satisfactory that it has confirmed the opinion that the method is the most satisfactory one for the work in hand, the nature of which has already been indicated.


Partial top view showing spring brushes on guide block.

End view of slider and cross section of rheostat.

Side view of one brush

FIG. 1.—*Details of construction of tubular rheostat*

III. FIELD RHEOSTATS

A full-size cross section of a field rheostat is shown in Fig. 1. The arrangement for leading the current in and out is also shown. Two lengths were used, 5.5 m for the motor-field rheostats and 12 m over all for the generator field rheostats.

Brass tubes were used, and the lengths were soldered end to end so as to make a perfectly smooth winding surface, a short sleeve being placed inside to make a good mechanical joint.

1. *Insulation.*—A coat of insulating varnish was applied to the tubes and allowed to dry. A 5 cm strip of varnished cambric was then wound on, after which another coat of the liquid insulator was applied and allowed to dry. This was followed by another coat each of varnished cambric and the insulating compound giving a smooth, hard surface on which to wind the wire. The resulting insulation was excellent, the completed rheostats showing 100 megohms or more, and each was tested at 1200 volts a. c. before being put into service.

2. *Winding.*—Enameled resistance wire was used, the enamel serving for the insulation between turns, which were wound snugly together so that the rheostat has a smooth, rigid surface. Splices were made by silver soldering the wires in butt joints. The winding was done on an extemporized lathe arrangement. After winding, the enamel was removed from the surface of the wire where the contact was to be made. In fact, a small amount of the metal was removed in order to slightly flatten the surface of the wires, and so improve the contact.

3. *Brushes, etc.*—As shown in Fig. 1, the contact brushes, which are laminated phosphor bronze springs, are carried on a sheet brass support which nearly surrounds the tube. Two brushes bear on the resistance winding, near the bottom, while a third, and longer brush, runs in a brass channel which serves as a return conductor. The channel is insulated from the winding by two layers of impregnated tape. The most satisfactory method of attaching the channel to the tube was found to be by pieces of thin silk tape placed at intervals along the tube, and each inserted under two or three turns of wire. This, of course, had to be done as the tube was being wound. These are tied to ears on the channel formed by sawing slots in the edge of the channel and bending out the strip between the slots.

4. *Mounting of Tubes.*—As shown in Fig. 2, the rheostats are mounted horizontally in a single tier, the operating motors being placed on a shelf at one end. They are placed near the ceiling of a long hallway into which the dynamo room opens, and so do not take up space useful for other purposes.

The motor end of each tube is clamped in position, but otherwise the tubes are supported on rollers to allow for expansion. Those rheostats which require water cooling have their ends connected by flexible copper tubes to provide for the water circulation.

5. *Cooling System.*—As already stated, artificial cooling is provided, wherever necessary, by circulating water through the brass tubes on which the resistances are wound. When first installed the city water supply was used, the small amount of water necessary for cooling being allowed to run to waste. Occasionally, however, under extreme atmospheric conditions, moisture condensed on the winding, and it was feared that the insulation might become injured. Accordingly, a closed circulation of the cooling water was substituted, a low-speed motor being directly connected to a gear pump. The motor is automatically started whenever a motor generator is operated whose field rheostat requires water cooling.

A vertical mounting of the tubes would be preferable in a building whose arrangement permitted it; as, for example, in a shaft large enough to allow of easy access. A simple thermal circulation of a cooling liquid would then be sufficient, the tubes being connected in parallel with one common return tube.

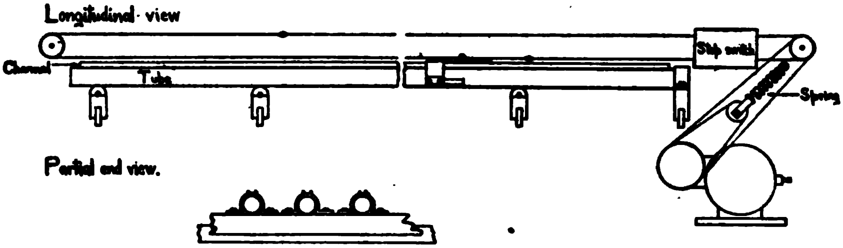


FIG. 2.—*Method of mounting tubular rheostats*

6. *Design of Windings.*—Preliminary experiments had shown that under working conditions settings could be made on a motor-operated slide-wire rheostat of the type described to about 1 mm, about the average diameter of the wire which it was found convenient to use in winding the rheostats. It was arbitrarily decided to make the sensitivity of setting on the generator rheostats approximately 0.01 volt per millimeter, or 10 volts per meter of length of rheostat.

In Figs. 3 and 4 are shown the design curves for a typical generator rheostat. The magnetization curve of the generator was experimentally determined in the usual way (curve 1). From this, the resistance of the field winding and the normal voltage of the source, curve 2 was calculated, showing the resistance in the rheostat as a function of the generated voltage. By scaling off tangents to curve 2, the ratio of a small change in resistance to

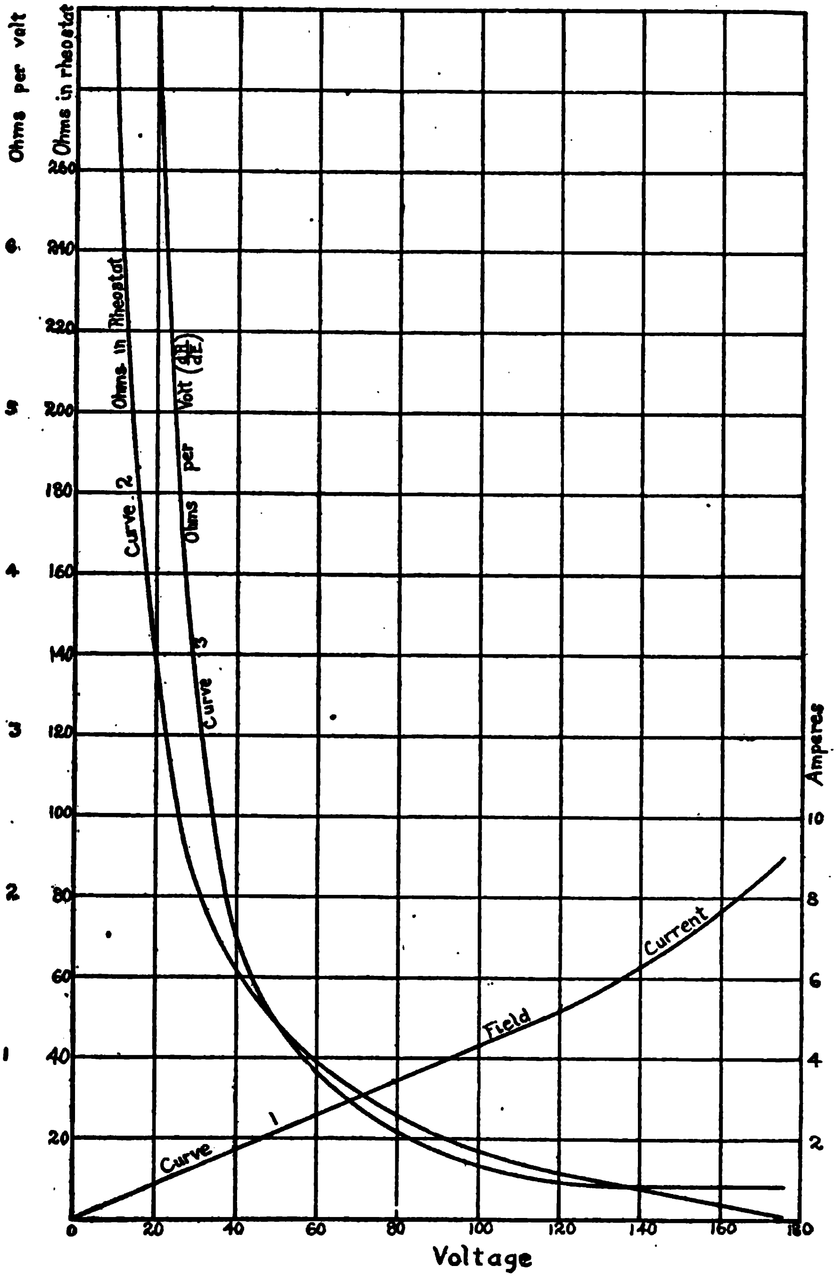


FIG. 3.—*Design curves for typical rheostat*

the resulting change in voltage can be determined. This is shown as ohms per volt in curve 3; but since each millimeter of the length of the rheostat represents a change of 0.01 volt in the generator voltage, curve 3 may be plotted in the form shown in curve 4 (Fig. 4) by merely a change of scale, giving the resistance of the rheostat per millimeter throughout its length.

From a consideration of the conditions to be met in all the field rheostats required in the system, the sizes of wire shown in the following table were chosen, somewhat arbitrarily:

TABLE 1

Wire Used for Winding Rheostats

Material	No. (A. W. G.)	Diameter	Resistance per turn
		Millimeters	
Copper	17	1.15	0.0021
Do	20	.81	.0043
Brass	17	1.15	.0075
Do	20	.81	.015
Do	22	.64	.023
18 per cent German silver	17	1.15	.034
Advance	18	1.02	.063
Do	21	.72	.13
Do	24	.51	.26

With the exception of the No. 22 brass, which was used only in two special rheostats, the wires are so chosen that the resistance per turn increases by a factor of about 2 from step to step, while the total change in diameter of wire is only slightly over 2 to 1.

The final data for the winding is shown by the broken line (No. 5) of Fig. 4, in which the horizontal steps indicate the lengths wound with the various sizes of wire. It will be noticed that the ideal curve does not cut the steps of the actual curve quite symmetrically. This is caused by slight arbitrary changes in design to adapt to materials, and also by the fact that the former is based on resistance per millimeter, the latter on resistance per turn. The final result is that settings can be made on the rheostat to an accuracy of about 0.02 per cent or better, since the mechanism allows the adjustment to be made, when necessary, to a single turn of wire.

The design of the motor field rheostats was much simpler, an untapered winding being found to be sufficient to secure a change of but 0.01 per cent in speed for a single turn of the wire on the rheostat. The motors are not of the interpole type, and rheostats 5.5 m long suffice to cover the safe range of speed, with the sensitivity just given.

IV. RHEOSTATS FOR THE CONTROL OF DIRECT CURRENT AND VOLTAGE

1. *Voltage Rheostats.*—These are identical in general construction with field rheostats already described. They are 7.5 m long and are wound with about 11 500 turns of No. 22 brass wire, giving a resistance of 254 ohms. Definite voltages from storage batteries (in multiples of 80, up to 320) are connected across the whole resistance and a variable voltage is tapped off by means of the sliding contact for use in testing. The current capacity of the rheostat is sufficient to allow enough current to be drawn from it for all ordinary work in instrument testing.

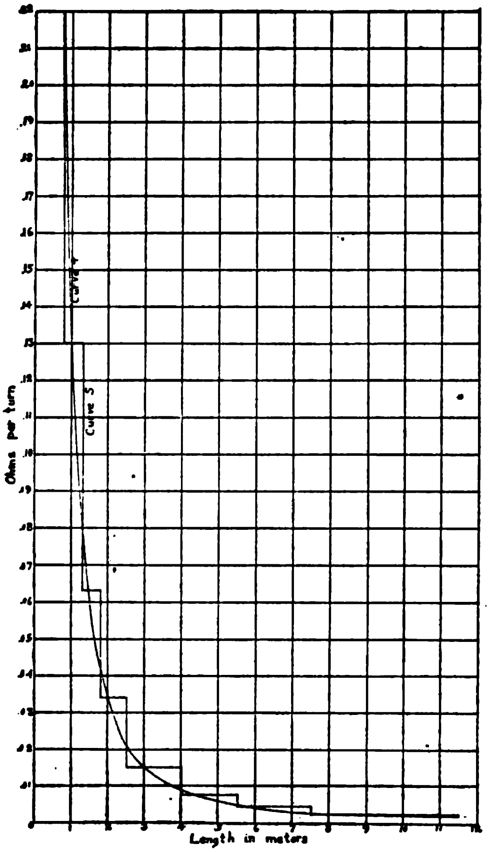


FIG. 4.—*Design curves for typical rheostat*

2. *Current Rheostats.*—Satisfactory current rheostats operating on a low voltage source and arranged to fit in with the same system of remote control have so far been worked out only for the larger ranges of current, from 300 up to 10 000 or 12 000 amperes.

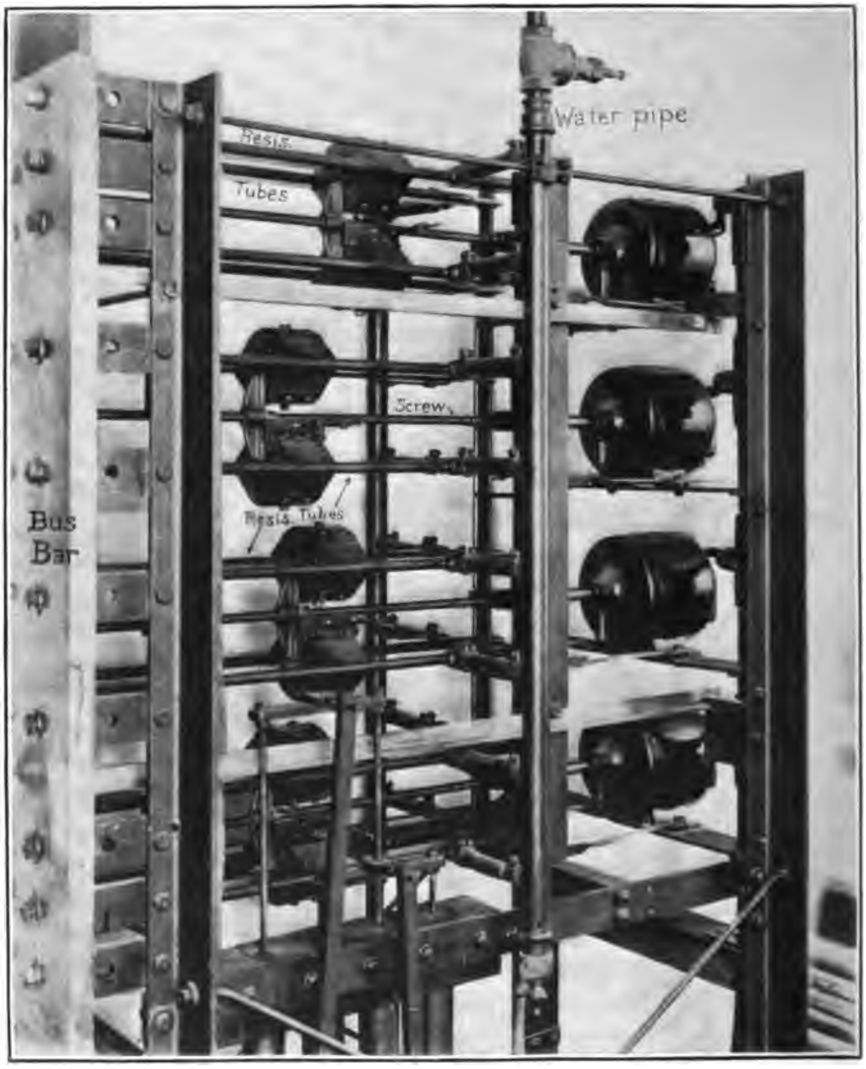


FIG. 6.—*General view of heavy current rheostat*

This rheostat, which was originally designed for hydraulic operation,[1] was rearranged so as to be operated by four 0.1 kw motors. The resistance elements are flattened tubes through which water flows for cooling. Contact is made directly on the tubes by heavy laminated copper brushes, of circuit-breaker construction. The tubes are arranged in four sets of four each. The four brushes of a set are rigidly connected together, and are propelled by a single screw on the shaft of a motor, as shown in Fig. 5.

The four tubes of three of the sets are connected in series parallel. Tubes *A* and *B* are in series, as are also *C* and *D*, while the two pairs of tubes are in parallel. All four sets of tubes are connected in parallel, but as at the end of their travel the brushes ride onto insulating strips, the circuit through any set may be broken.

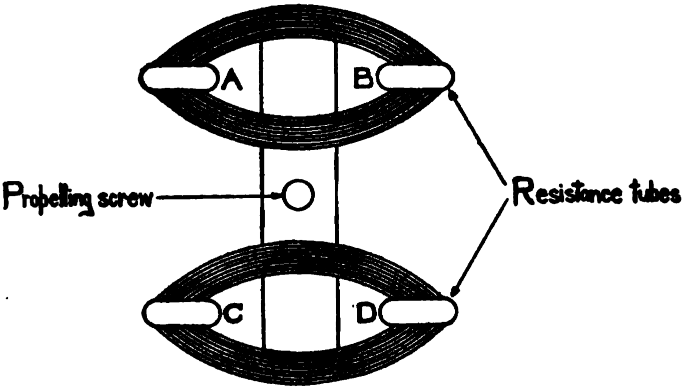


FIG. 5.—*Arrangement of brushes and resistance tubes of heavy-current rheostat*

In order to extend the range of the rheostat downward the tubes of the fourth set are all connected in series, making the resistance of this set four times that of each of the other three. For still smaller currents, the brushes of all four sets are run out to the open points and a hand-operated rheostat is connected in parallel.

The operation of the motors is precisely the same as for the other parts of the control system, two speeds giving coarse and fine adjustment, etc. In fact, the control wiring is entirely symmetrical with that for the field rheostats. A general view of the complete rheostat is shown in Fig. 6.

---

[1] The main portions of the rheostat were designed several years ago by E. B. Rosa, H. B. Brooks, and F. S. Durston, and built in the instrument shop of the Bureau of Standards by Joseph Ludewig.

V. PHASE CONTROL

Use is made of two well known methods of phase control. The more satisfactory one is by the use of two similar alternators on the same shaft, one being used as a source of current and the other as a source of voltage, the phase adjustment being made by shifting the angular position of the stator armature of one alternator. In the other method the adjustment is accomplished by slowly moving the rotor of a phase-shifting transformer. In either case the motion is accomplished by a small motor actuating a compound worm drive.

This arrangement also fits in very nicely with the other parts of the motor-generator control, the two speeds giving coarse and fine adjustment of the phase relation.

VI. OPERATING DETAILS

1. *Motors.*—In order to operate satisfactorily at widely different speeds, a fairly high-speed motor has been found to be most satisfactory. The motors used are of the Eck worm-geared type, one-sixth hp 2500 rpm, worm geared in the ratio of 46 to 1, and arranged to rotate in either direction. For full speed 120 volts are applied to the armature, and for slow speed 10 volts. On account of the resistance of the armature, the ratio of the speeds is, however, greater than the ratio of the voltages, being about 18 or 20 to 1, instead of 12 to 1.

2. *Power for operation.*—The low speed can not be obtained merely by inserting resistance in the armature circuit, since the starting torque is then entirely too small for satisfactory operation. A small 20-volt, 3-wire storage battery is used to provide the low speed. The neutral of this battery is connected to the neutral of the regular 240-volt, 3-wire d. c. supply, thus forming a modified 5-wire system.

The arrangement is shown in Fig. 7, from which it is easily seen that a 2-speed, 2-direction control is obtained from the 4 contact positions of the controller.

3. *Controllers.*—As shown in Fig. 8, the controller for operating a motor-generator set has five levers, one each for frequency, phase, the fields of two generators, and an auxiliary d. c. voltage. The two inner contacts are for low speed and the two outer ones for high speed, and the normal position of the spring levers is at the center with the circuit open. In all cases the connections are such that motion to the right raises voltage or frequency, while

motion to the left causes a corresponding lowering. Accordingly, a small displacement to the right causes a very slow increase in voltage or frequency, and a further motion to the right against the stop gives a rapid increase. Similarly, slow and rapid decreases are obtained by motion to the left.

The springs controlling the levers are small helical springs, wound so as to be under an initial tension. The handles are removable, so that the danger of accidentally closing circuits not in use may be avoided.

Excepting where used at fixed "set-ups," the controllers are portable and are provided with flexible leads so that they may be placed wherever the convenience of the work demands, and they are all interchangeable.

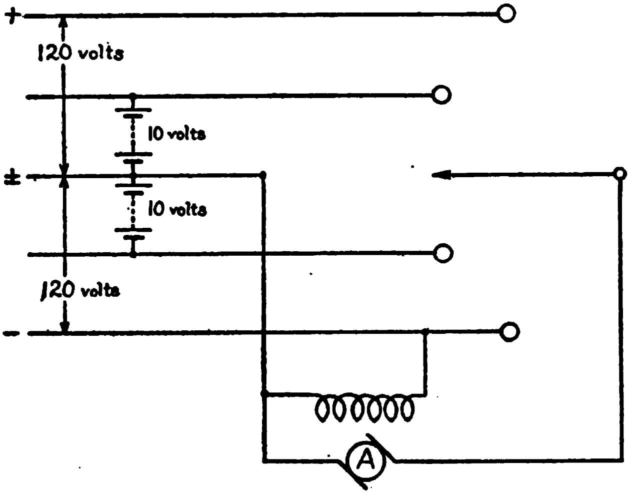


FIG. 7.—*Method of obtaining 2-direction, 2-speed control from 5-wire system*

4. *Jacks.*—To provide a controller at each outlet for each motor-generator set would be too complicated and inconvenient. Hence, only one controller is used at an outlet, and it is arranged so as to control the output of any motor generator desired by merely plugging in two jacks, one connecting to the source of power and one connecting to the control motor armatures. This arrangement is indicated in Fig. 8. A commercial telephone jack is used, somewhat modified to adapt it to the required conditions.

The fixed parts of the jacks are mounted directly on the special conduit containing the wiring.[3]

---

[3] For a brief description of the electrical distribution and general laboratory arrangements for the building, see P. G. Agnew, Elec. Rev. and West. Electrician, 64, pp. 811, 820; 1914.

5. *Automatic Stop Switch.*—It is necessary to have some automatic device to limit the travel of the brush at the ends of the rheostat, as otherwise the motor would stall and fuses blow or injury to the apparatus result. Merely an automatic switch to open the armature circuit is not feasible, as this would make the whole device inoperable whenever a brush accidentally reached the end of the rheostat adjustment. At first a simple friction drive was tried, so that the pulley or cord would slip when the brush reached the end, but this arrangement did not prove to be satisfactory. The switch indicated in Fig. 9 has, however, been entirely satisfactory.

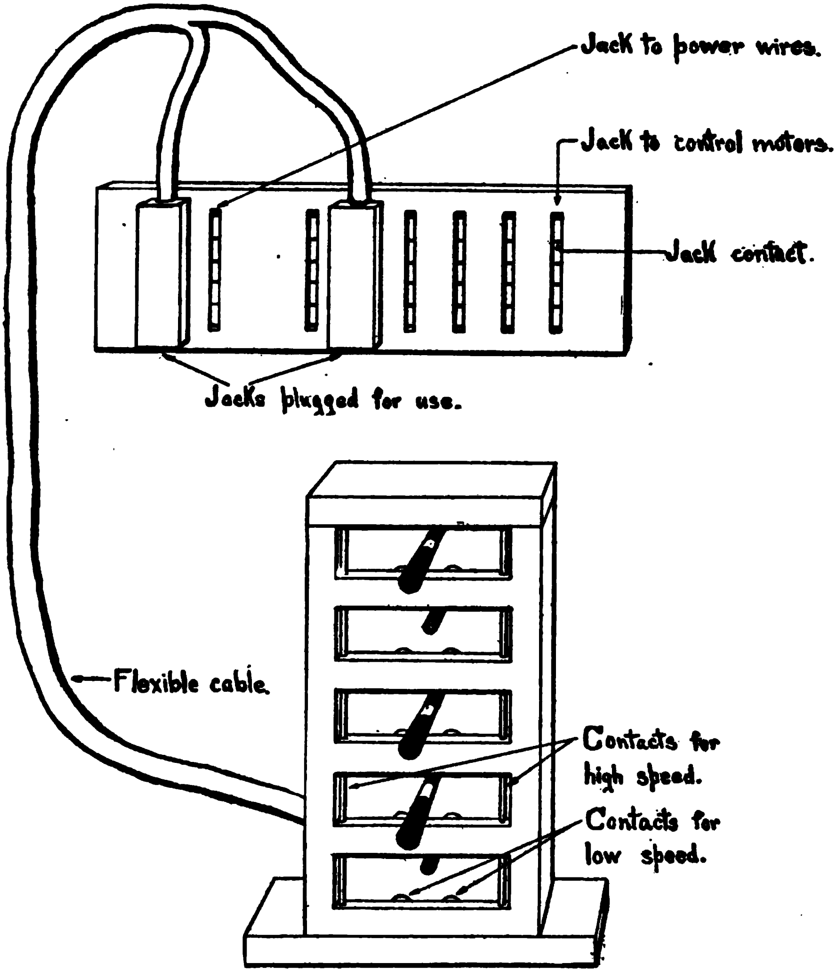


Fig. 8.—*Controller and jacks*

As the rheostat brush reaches the end of its travel, a small brass bob, *B*, attached to the cord which operates the brush, enters the space between a fixed brass bar, *F*, and a spring, *S*, opening the circuit at *K*, thus stopping the motor. But *B* makes electric contact between *F* and *S*, completing the circuit through *R* to the positive side of the line, so that by throwing the controller lever to the negative side of the line the motor will rotate in the opposite direction, thus moving the brush toward the other end of the rheostat. When the brush reaches the other end of the rheostat, a second brass bob on the lower section of the cord enters the lower part of the switch, and the operations are precisely like those just described for the upper part of the switch.

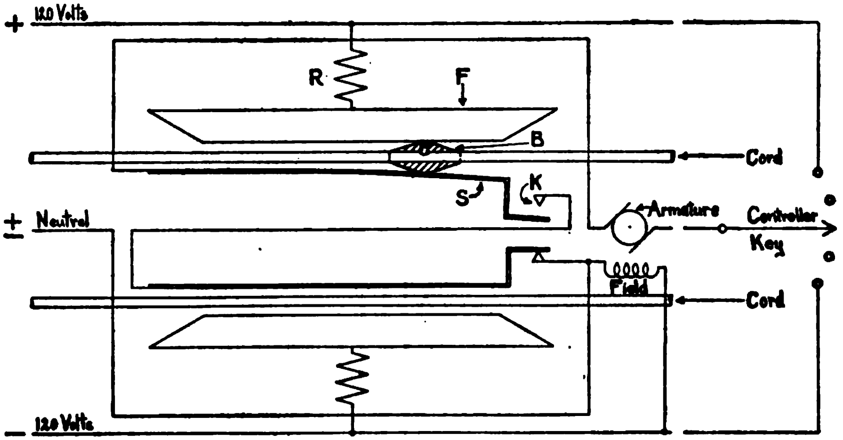


FIG. 9.—*Details of automatic stop switch*

6. *Wiring.*—The wiring is surprisingly simple. In addition to the four power wires (the neutral is not necessary at the controller stations) only one wire for each control has to be carried around the laboratories—that is, one wire for each motor armature. In the original installation there were 17 controls, and therefore 17 motors, and but 21 wires were necessary. Only one additional wire is required when an additional control is added.

In the general wiring diagram, Fig. 10, the complete connections for one motor-generator set are shown with jacks at a controller station, together with one controller.

7. *Motor Fields.*—The four control motors required for the complete control of a motor-generator set have their fields connected in parallel, and the switch controlling their fields is placed on the panel from which the motor-generator set is started. The

closing of this switch thus becomes a part of the process of starting the set.

VII. EXPERIENCE WITH SYSTEM

In over two years' operation the system has given very little trouble—much less than was anticipated. The cords gradually stretched slightly and had to be tightened once or twice, and a few very slight changes have been made in details of design or construction as experience has suggested them. Otherwise the whole system has required little more attention than would ordi-

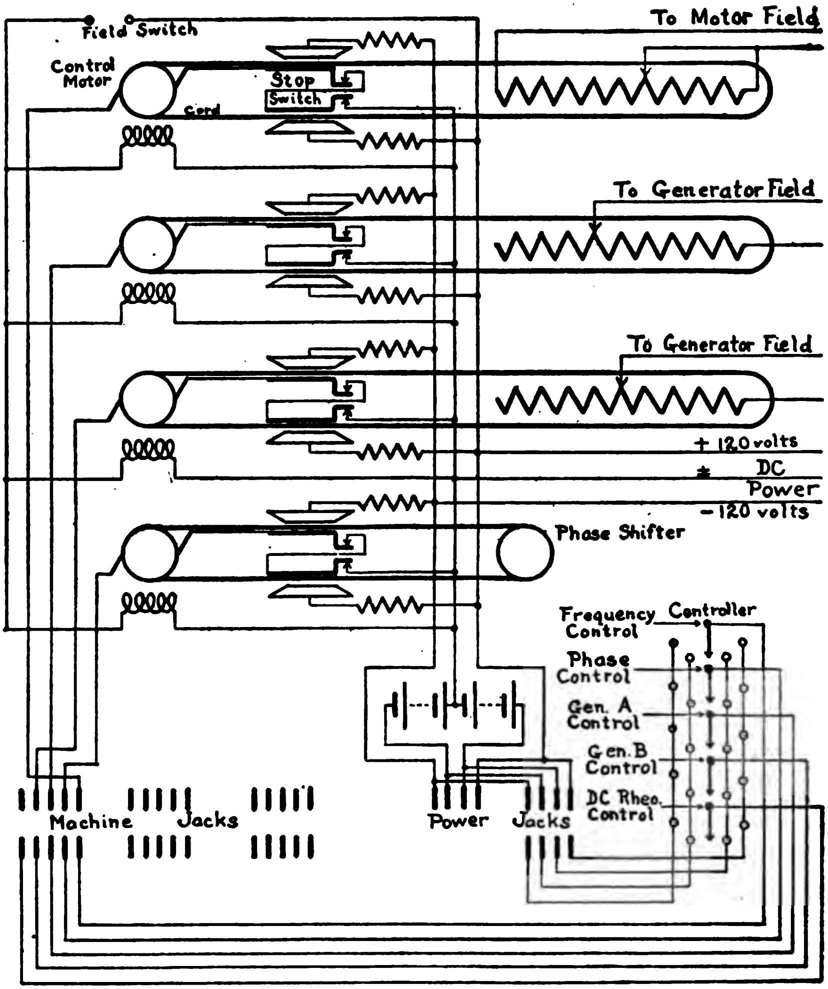


FIG. 10.—*General wiring diagram, showing details for complete control of one motor-generator set, with controller, and jacks for plugging so as to control other sets*

narily be expected in the use of the same number of small motors in a laboratory.

There is a slight amount of backlash, due to the elasticity of the cord, but it is not at all serious, amounting to only about 0.1 or 0.15 per cent on the average.

One limitation that has sometimes proved inconvenient is that care has to be exercised in the use of an a. c. generator with so wide a range of field excitation not to draw too much current at low excitation, else the armature reaction may cause wave-form distortion. For this reason it is not permissible to draw full-load current at very low excitations if purity of wave form is important. The admittance of the connected load is a more logical basis for determining the permissible generator load than is the armature current.

The simplicity and convenience of the system, both in testing and in investigational work, has greatly increased the efficiency of the work of the laboratory, frequently saving the time of one observer.

WASHINGTON, May 26, 1916.

INTERNATIONAL SYSTEM OF ELECTRIC AND MAGNETIC UNITS

By J. H. Dellinger

CONTENTS

Page

I. Introduction 599

II. The international system 600

1. Simplicity of this system 604
2. Subordination of the magnetic pole 605
3. Limitation to electromagnetism 605

III. The magnetic quantities 606

1. The magnetic circuit 607
2. Induction and magnetizing force 608

IV. Rationalization of the units 613

1. The Heaviside system 613
2. Other attempts to eliminate 4π 616
3. The two sets of magnetic units 621
4. The ampere-turn units 623

V. Summary 628

Appendix.—Symbols used 631

I. INTRODUCTION

Electric units and standards are now very nearly uniform in all parts of the world. As a result of the decisions of international congresses and the cooperation of the national standardizing laboratories, the international ohm and ampere are accepted everywhere as the basis of electrical measurements. A complete system of electric and magnetic units is in general use, built upon these fundamental units. There have been proposals to change the units from time to time, and as a result there is some diversity of usage in respect to units in current electric and magnetic literature. For instance, Heaviside units are used in certain recent books on theoretical electricity; a slight change of electric units is advocated by M. Abraham; and quite a number of different magnetic units are used in presenting the results of magnetic experiments. It appears worth while to examine critically the system of units which is generally used, to study the reasons which are advanced for changes in the system, and to inquire whether any of the various proposed units offer advantages which would justify the trouble and confusion incident to a general change of units.

The units actually used in electrical measurements are based on certain fundamental electrical standards which were so defined as to represent, as closely as experimental evidence permitted, the theoretical electromagnetic units. The units of the various electric quantities are derived from the fundamental units in accordance with the equations of ordinary electrical theory, and in consequence the units actually used in practice are all very close representatives of the corresponding electromagnetic units. The electromagnetic system is familiar, having been frequently described. The units used in practice to represent the electromagnetic units have been called the international units. The very slight differences in magnitude between the international and the corresponding electromagnetic units are determined by absolute measurements made from time to time. (The present values of these differences are given, on the basis of recent absolute measurements, in this Bureau's Circular No. 60, Electric Units and Standards.) The system of international units will be discussed here in some detail before treating the various proposals which have been made for changes in the units. The said proposals would apply both to the electromagnetic units and to the international units, their representatives.

II. THE INTERNATIONAL SYSTEM

Every complete system of electric units requires four fundamental units instead of only three, as in mechanics. The necessity for the one additional unit arises from the fact that the identity of mechanical and electrical phenomena has not been established. Of the four quantities taken as fundamental (*a*) three may be mechanical and one electrical, or (*b*) two mechanical and two electrical, or (*c*) one mechanical and three electrical, the only theoretical requirement being that both mechanical and electrical quantities be represented among the four. Thus, very many systems are possible. No systems of type (*c*) are in use, although they can be very easily made up, and are not at all grotesque—for example, a system using R, I, μ, and T as fundamental.

The electrostatic and electromagnetic systems are of type (*a*). The fundamental units in each of these systems are those of length, mass, time, and a property of the eletromagnetic medium. The property of the medium utilized is the dielectric constant in the electrostatic system and magnetic permeability in the electromagnetic system. For convenience, zero dimensions are sometimes assigned to the property of the medium in writing dimensional formulas, but it remains none the less a fundamental quantity of the system.

The international system is of type (*b*). In the definitions adopted by the London Electrical Conference of 1908 two electric units were defined in terms of specified standards—the international ohm and the international ampere. These two, plus units of length and time, may be regarded as forming the basis of a distinct system, and they have been so considered by a few writers. This system is very convenient in electrical work, although it has no value or utility in mechanics or other parts of physics. The system is centered around the phenomena of electric current. Electric current is more familiar and of vastly greater practical importance than electrostatic charges or magnetic poles, upon which the other two familiar systems are based. This is one of the reasons why the international system is the most convenient and the most used electrical system.

Only eight units (the international ohm, ampere, volt, coulomb, henry, farad, joule, and watt) have been defined by international congresses, and it is desired to show that these units form part of a distinct and complete electrical system. That the international units form a system distinct from all others may be seen from the following considerations. The international units are historically based upon the "practical" electromagnetic units, as has been stated above. However, two of the international electric units are defined in terms of arbitrary standards and hence are independent or arbitrary [1] units, viz, the international ohm and the international ampere. Since a complete system of electric units requires four independent units, only two additional units are needed. Therefore the international system can not have all four of the fundamental quantities of the electromagnetic system, viz, length, mass, time, and magnetic permeability. The two of these quantities which are needed to complete the international system are length and time. Both length and time enter essentially in the fundamental relations between the important electromagnetic quantities. (This is clearly exhibited in Table 1 below.) Mass does not enter at all into those relations, and magnetic permeability is a subordinate quantity in this system just as it is in the electrostatic system.

---

[1] The international ohm and ampere are independent units in spite of the fact that in the realization of the standards by means of which they are defined other physical quantities are utilized. The international ohm is defined as the resistance of a uniform column of mercury of specified length and mass. This length and mass, however, are merely auxiliary to the preparation of the standard. The unit is the actual resistance of such a standard, and its magnitude would not vary if different units of length and mass were used in the definition of the standards. The case is very similar to the definition of the unit of temperature on the international hydrogen scale. This is strictly an arbitrary unit, and yet in its definition (see this Bulletin 3, p. 664; 1907) use is made of the meter to specify the initial pressure in the hydrogen thermometer.

That the international units form a complete electrical system, which is in fact the system commonly used, is brought out by Table 1, in which the units of the principal electric and magnetic quantities are derived from the units of resistance, current, length, and time by the use of the ordinary equations of electrical theory. The international volt, coulomb, etc., were thus derived from the international ohm and ampere and the second in the definitions adopted by international congresses. Each unit in this system is the representative for practical purposes of the corresponding unit in the electromagnetic system and differs from it only very slightly. The small differences between the units in the two systems are determined by absolute measurements made from time to time.

This mode of definition was thus extended to the whole system of electric and magnetic units by Prof. V. Karapetoff in the appendixes of his books, The Electric Circuit (1912) and The Magnetic Circuit (1911). He calls the units so obtained the "ampere-ohm system." In his derivations, however, he uses some equations differing by the factor 4π from the classical equations. Certain of the units thus derived are therefore not representatives of the corresponding electromagnetic units. Consequently his ampere-ohm system is not quite the same as the "international system" as interpreted herein. The Karapetoff units are discussed on page 620 below.

The table gives the dimensional formula for each quantity, as well as the defining equation or equation which gives the mathematical relation of the quantity to previously defined quantities. All the symbols used are defined in the table, except the following, which are introduced without definition: L = length, T = time, R = resistance, I = current, N = number of turns, S = area, s = length along a path.

TABLE 1

The International System

Quantity	Symbol	Unit[a]	Defining equation	Dimensional formula
Electromotive force	E	Volt	$E=RI$	$[E]=[RI]$
Quantity of electricity	Q	Coulomb	$Q=\int Idt$	$[Q]=[IT]$
Electrostatic capacity	C	Farad	$C=\frac{Q}{E}$	$[C]=\left[\frac{T}{R}\right]$
Dielectric constant	K		$C=\frac{KS}{4\pi l}$ (for a parallel plate condenser of large area S).	$[K]=\left[\frac{T}{LR}\right]$
Electric field intensity	$\mathcal{E}$	Volt per cm	$\mathcal{E}=\frac{dE}{ds}$	$[E]=\left[\frac{RI}{L}\right]$
Electric displacement	D	Coulomb per cm².	$D=\frac{K}{4\pi}\mathcal{E}$	$[D]=\left[\frac{IT}{L^2}\right]$
Self-inductance[b]	$\mathcal{L}$	Henry	$\mathcal{L}=\frac{E_1}{dI_1/dt}$	$[\mathcal{L}]=[\mathfrak{M}]=[RT]$
Mutual inductance [c]	$\mathfrak{M}$	Henry	$\mathfrak{M}=\frac{E_2}{dI_1/dt}$	
Magnetomotive force	$\mathfrak{F}$	See Table 6	$\mathfrak{F}=\frac{4\pi}{10}NI$	$[\mathfrak{F}]=[I]$
Magnetizing force [d]	H	do	$H=\frac{4\pi NI}{10L}$	$[H]=\left[\frac{I}{L}\right]$
Magnetic flux [e]	ϕ	do	$\phi=10^8\int_0^t Edt$	$[\phi]=[RIT]$
Magnetic induction	B	do	$B=\frac{d\phi}{dS}$	$[B]=\left[\frac{RIT}{L^2}\right]$
Permeability	μ	do	$\mu=\frac{B}{H}$	$[\mu]=\left[\frac{RT}{L}\right]$
Reluctance	$\mathfrak{R}$	do	$\mathfrak{R}=\frac{\mathfrak{F}}{\phi}$	$[\mathfrak{R}]=\left[\frac{1}{RT}\right]$
Intensity of magnetization.	J	do	$B=B_0+4\pi J$	$[J]=\left[\frac{RIT}{L^2}\right]$
Magnetic susceptibility	κ	do	$J=\kappa H$	$[\kappa]=\left[\frac{RT}{L}\right]$
Magnetic pole strength[f]	m	do	$\phi=4\pi m$	$[m]=[RIT]$

[a] The names of these units are strictly the "international volt," "international coulomb," etc., but in practice "international" is omitted.

[b] In the definition of self-inductance, E_1 is the emf created in a circuit by the variation of the current I_1 in the same circuit.

[c] In the definition of mutual inductance, E_2 is the emf induced in a circuit by the variation of the current I_1 in another circuit.

[d] H in the defining equation is the magnetizing force at the center of a very long solenoid of N turns and length L.

[e] ϕ in the equation is the change of flux in the time t giving rise to the emf E in a closed circuit linking with the flux.

[f] ϕ in this equation is the total magnetic flux emanating from or associated with magnetic poles of aggregate pole strength m; it is strictly equal to the resultant flux through the magnet only when the magnet is very long and thin.

1. SIMPLICITY OF THIS SYSTEM

We build up our electrical equations and make measurements in terms of resistance, current, length, and time. It is entirely legitimate to write dimensional expressions in terms of these quantities. The dimensional formulas in the international system of electric units, in fact, give expressions which are as simple and as helpful in electricity as the usual dimensional expressions in length, mass, and time are for mechanical quantities. This advantage is decidedly lacking in the electrostatic and electromagnetic systems. The superiority of the international system in this respect is clearly shown by an example. The dimensional formula for magnetic field intensity or magnetizing force is

$$[H]=\left[\frac{I}{L}\right]$$

This gives as clear and simple a statement of the relations of the two electromagnetic quantities, H and I, as the dimensional formula for force, below, gives for mechanical quantities. Compare with the dimensional formula for H. in the electromagnetic system:

$$[H]=\left[\frac{M^{1/2}}{L^{1/2}T\mu^{1/2}}\right]$$

This is not convenient as regards the conveying of physical information. The point is that it bears no direct relation to the actual working equations of electricity. In the ordinary systems of mechanical units, the dimensional equations are almost the same as the defining equations of mechanical units. Thus the dimensional equation of force, $[F]=\left[\frac{ML}{T^2}\right]$, is similar to $F=M\frac{d^2L}{dt^2}$. Similarly, in the international system of electric units the dimensional equations are similar to the defining equations, which are the common equations of practice—for example, $[H]=\left[\frac{I}{L}\right]$ is closely related to $H=\frac{2I}{r}$, which holds for an infinitely long, straight conductor.

The various dimensional formulas in the table very simply suggest the ordinary equations of electrical theory and practice. Take, for instance, $[D]=\left[\frac{IT}{L^2}\right]$. The functioning of electric displacement is at once apparent, for since $[IT]=[Q]$, it is suggested that electric displacement is quantity per unit area. The formulas $[C]=\left[\frac{T}{R}\right]$ and $[\mathfrak{L}]=[RT]$ are very closely related to the expression for impedance

$$Z=\sqrt{R^2+\left(\frac{2\pi\mathfrak{L}}{T}-\frac{T}{2\pi C}\right)^2}$$

where T is the period of alternation. The dimensional formulas for K and μ are both closely related to actual methods of measurement. K depends on capacity $\left[\frac{T}{R}\right]$ and linear dimensions $[L]$. μ may be determined by the measurement of a self-inductance $[RT]$ and linear dimensions $[L]$ of a coil. It of course follows from $[K]=\left[\frac{T}{LR}\right]$ and $[\mu]=\left[\frac{RT}{L}\right]$ that $\left[\frac{1}{K\mu}\right]=\left[\frac{L^2}{T^2}\right]$, the familiar equation suggesting the influence of K and μ upon the velocity of wave propagation.

2. SUBORDINATION OF THE MAGNETIC POLE

One of the advantages of the international system is that it does not give undue prominence to magnetic pole strength. The complexity of the dimensional expressions of the electromagnetic system and its poor correspondence to the conditions of practice are in part due to its being based upon an unimportant phenomenon. Magnetic poles are of little theoretical or practical importance, while magnetic flux, field intensity, etc., are. The medium is the important thing, as shown by Faraday and Maxwell. Magnetism is becoming more and more regarded as one kind of manifestation of electricity. In the table of the international system given above, magnetic pole strength was defined last, showing that all the other magnetic quantities are definable independently of it. (It can be similarly subordinated in the equations of the electrostatic system.) A free magnetic pole does not exist in nature, magnetic pole strength does not appear in engineering formulas, and it is consequently a satisfaction to find that it can be dispensed with in the theory also.

3. LIMITATION TO ELECTROMAGNETISM

The international electrical system of dimensional equations is not suitable as a basis for all physical quantities. It gives dimensions as awkward for the quantities of mechanics as the electromagnetic system gives for electrical quantities, and is therefore not of such general application as the systems in which length, mass, and time are fundamental. The dimensions of mechanical quantities in this sytem are readily obtained as follows: Energy is the quantity common to electricity and mechanics, and it has the simple dimensions $\left[R\,I^2\,T\right]$. From the relation $\left[\frac{M\,L^2}{T^2}\right]=\left[R\,I^2\,T\right]$, the dimensions of mass and other mechanical quantities may be derived. Such dimensional expressions of mechanical quantities have no convenience or value. Furthermore, the unit of mass comes out 10^7 g and the unit of force 10^7 dynes, similarly to the unit of energy which is 10^7 ergs (1 joule). The international electrical system is valuable simply as a practical convenience in dealing with electrical phenomena. It can not be thought of as supplanting the classical system based on length, mass, and time, since the international ohm and ampere are not as fundamentally important as the kilogram and meter.

III. THE MAGNETIC QUANTITIES

The electrostatic and electromagnetic systems are primarily systems of physical quantities rather than units, and upon them various systems of units are based. Thus, for instance, both the cgs and the "practical" electromagnetic systems of units are in use. These differ in the particular units chosen for the fundamental quantities. In the case of the international electric units, only one particular set of units is used for the fundamental quantities; the four fundamental units are the international ohm, the international ampere, the centimeter, and the second. The defining equations given in Table 1, above, for E, Q, C, $\mathcal{L}$ and $\mathfrak{M}$, are those by which the international units of these quantities were derived by international congresses. The only electric unit defined by the equations of Table 1 that is not in use is the unit of dielectric constant. This would be expected, as the corresponding electromagnetic unit is never used, the electrostatic unit being universally employed. With this exception, the particular units indicated in Table 1 are the ones most commonly used. The units of the electric quantities correspond in magnitude to the "practical" electromagnetic units, and the magnetic units derived by the equations given in the table correspond to the cgs electromagnetic units. In addition to these magnetic units certain others are widely used. The latter units are the ampere-turn and units related to it. These units may be shown to constitute a complete alternative set of magnetic units, their use requiring certain of the equations to be changed by the factor 4π. The two sets of magnetic units are compared in Table 6 below.

Magnetic units involving the inch as the unit of length are also in use, particularly when the results of measurements are presented in the form of curves. While it would be possible to build up a definite system using the inch as the unit of length, these units are usually regarded as isolated units. When used in equations, they are accompanied by suitable numerical factors.

The nomenclature of the magnetic units is somewhat unsatisfactory. For instance, in the first set of magnetic units just referred to, at the present time the name "gauss" is applied both to the unit of induction and the unit of magnetizing force. In order to bring out clearly the difference between these two quantities, some general considerations regarding the magnetic circuit will be given here.

1. THE MAGNETIC CIRCUIT

A tube of magnetic induction is analogous to a tube of electric displacement, and also to a path along which electric current flows. The analogy is very close except that permeability and reluctance are not constant in magnetic material. The strictness of the analogies between electric and magnetic quantities is shown by the following table:

TABLE 2

Comparison of Magnetic and Electric Quantities

[See appendix at the end of this paper for symbols]

	In a circuit	At a point in a medium
Magnetism	$\phi=\frac{\mathfrak{F}}{\mathfrak{R}}$	$B=\mu H$
Electric current	$I=\frac{E}{R}$	$U=\gamma\mathcal{E}$
Electrostatics	$Q=CE$	$D=\frac{K}{4\pi}\mathcal{E}$

The analogy between the magnetic and the electrostatic relations is much better than that between magnetism and electric current in fact although not in form. There is no phenomenon of magnetic conduction corresponding to electric conduction, whereas magnetic induction and electric displacement are similar phenomena subject to the same laws. Reluctance is strictly analogous to the reciprocal of capacity; this is suggested in the name elastance, which Heaviside gave to the reciprocal of capacity. The first and third equations in the last column are similar except for the factor 4π, which is without physical significance; in fact, this dissimilarity is merely a peculiarity of one set of magnetic units.

The only vector quantities in the table are B and H and their analogues, D and $\mathcal{E}$ and U and $\mathcal{E}$. Magnetomotive force $\mathfrak{F}$ and electromotive force E are line integrals of the two field intensities, H and $\mathcal{E}$, respectively.

The term "magnetomotive force" (mmf) has been restricted by some writers to mean the total line integral of H along a closed path. It would thus have a value different from zero only when the path of integration links with electric current. The line integral of H along a part only of a closed path was called magnetic potential difference (mpd) or magnetic potential drop, or even magnetomotive force drop. According to these conventions, while a magnetic potential difference exists between the poles of a permanent magnet, yet one could not speak of a magnetomotive force due to the magnet, because the mpd between the poles in air is equal and opposite to the mpd within the magnet. If the term "electromotive force" were similarly restricted, there could be no emf due to a battery or a charged condenser.

Magnetomotive force is in fact the exact analog of electromotive force and bears the same relation to magnetic potential difference as emf does to electric potential difference. The potential difference between two points is the work done in carrying unit charge from one point to the other. The potential difference between the ends of any portion of a circuit is equal to the difference between the emf (or mmf) produced in that portion, by any causes whatever, and the emf (or mmf) expended in that portion.

2. INDUCTION AND MAGNETIZING FORCE

It is common practice in electrical engineering to use the name "gauss" both for the unit of magnetic induction and the unit of magnetizing force. This usage is recognized by the American Society for Testing Materials,[2] and provisionally by the American Institute of Electrical Engineers.[3] If induction and magnetizing force be looked upon as the same physical quantity, it is natural and unobjectionable to express them in the same unit. This view has been a consequence of the importance hitherto assigned to the magnetic pole. Thus, induction and magnetizing force may be looked upon as having the same physical nature when magnetizing force is defined as the force on a unit magnetic pole in a medium and induction as the force on a unit magnetic pole in a very short, wide cavity with its width perpendicular[4] to the direction of magnetization of the medium. There are, however, objections to this conception of induction, which will be pointed out below.

---

[2] Yearbook, p. 195; 1915.

[3] Standardization Rules, Rule No. 90; 1915.

The electromagnetic units were so chosen that μ_0 (permeability of empty space) $= 1$. This simplifies certain calculations. Thus, letting $B_0 =$ induction in a nonmagnetic medium, the equation $B_0 = \mu_0 H$ may be written $B_0 = H$ in electromagnetic units. Also, the equation $B = B_0 + 4\pi J$, of Table 1, is often written $B = H + 4\pi J$ in electromagnetic units. The numerical equality of H and B in nonmagnetic media, and the appearance of B and H as terms in the same equation, both tend to encourage the idea that they are of the same physical nature. A corollary of this idea is that permeability is a mere numerical ratio and not a physical quantity. The equations $B_0 = H$ and $B = H + 4\pi J$ do not hold in units other than electromagnetic, as will be shown in Section IV.

Arguments from the dimensions of the quantities have frequently been adduced in attempts to settle this question concerning the units of B and H. It has been maintained, on the one hand, that B and H are dimensionally identical in the ordinary electromagnetic system (μ suppressed), and are therefore expressible in the same unit; and, on the other hand, that when μ is retained as one of the fundamental quantities of the electromagnetic system, B and H are dimensionally different and therefore can not be expressed in the same unit. The question of the "gauss" has recently been discussed from this latter standpoint in an interesting article by M. Ascoli. (See footnote 16, p. 619.) Such arguments are certainly not conclusive. Dimensional identity or difference tells nothing about the physical difference between two quantities. The argument that dimensional identity indicates physical identity is refuted by the example of energy and torque. Who would measure torque in joules or calories? To maintain, on the other hand, that dimensional difference proves physical difference is not conclusive, as illustrated by the very fact that the two sets of dimensions, the electrostatic and electromagnetic, apply to every electric quantity. Dimensions are matters of convenience, and dimensional arguments can no more settle a question of the physical nature of a quantity than mathematical convenience can justify the physical identification of lines of magnetic force and lines of magnetic induction. Inasmuch as dimensional reasoning has been considered by various writers to be valid to decide the physical relation of B and H, it is thought worth while to consider further in this paper the actual physical nature of the two quantities.

---

[4] Maxwell, Electricity and Magnetism, par. 400.

There are a number of reasons for considering induction and magnetizing force to be different in physical nature, just as the deflection of a spring is physically different from the mechanical force producing it. As the names of the two quantities suggest, B characterizes the magnetized state of the medium and H is the agency tending to *produce* a magnetized state. Perhaps the distinction is most clearly seen by the analogies furnished in the discussion of the magnetic circuit (preceding section). There is no confusion between D, the electric displacement, which characterizes a state of the medium, and $\mathcal{E}$, the electric field intensity which produces the displacement. The distinction is even clearer between U, the current density in a medium, and the $\mathcal{E}$ which causes it.

Another analogy which points to the physical distinctness of B and H and to μ as a physical property rather than a mere numerical ratio is based on the energy of the medium. The various kinds of energy are each the product of two factors. Energy may be a force × a distance, a mass × half the square of a velocity, a pressure × a volume, etc. The energy density of an electrified medium is proportional to $D\mathcal{E}$, and of a magnetized medium is proportional to $\int HdB$. The energy density of a magnetized medium may be written (where μ is constant[5]) as $\frac{1}{8\pi}\mu H^2$. If μ were a mere numerical ratio, the magnetic energy density would involve a "generalized" force without the corresponding "flux." This would be contrary to the usual dynamical ideas.

Again, μ is one of the two quantities (μ and K) which are effective in the propagation of electromagnetic waves. Therefore μ must be an actual physical property (for two physical properties are dynamically necessary in a medium for the propagation of waves) unless K involves both properties. If electricity is of dynamical nature, therefore, either μ or K must be a physical quantity and both may be.

---

[5] Since μ is not constant for magnetic materials, the usual expression for the energy density is not very useful. The correct expression is in the integral form. Most reference books fail to emphasize this sufficiently.

In a number of respects B and H are of quite a different character. At the surface of separation between two media only the normal component of B is continuous, while only the tangential component of H is continuous. It is possible for induction to exist in a material with no magnetizing force. An example of such a case is a permanent ring magnet with no applied H, in which, therefore, $H = o$ and B is finite. (An interesting electrical analog of this is Kammerlingh Onnes's electrical conductor at a temperature very near the absolute zero, in which there was a current with no electromotive force.)

The point under discussion may be considered from the standpoint of convenience. While the conception of B and H as physically equivalent was found desirable in magnetic theories based upon magnetic poles, it is not so useful when the relations of magnetism to electricity are dealt with. While a given H is associated with a given current, it is B that is concerned in the phenomenon of induced electromotive force; that is, induced electromotive force depends on the medium, while current and its accompanying H are independent of the medium. Since these relations are at the basis of most magnetic practice, it is just as desirable to consider B and H to be different quantities as electromotive force and current.

If it be agreed, in accordance with the foregoing considerations, to look upon B and H as physically distinct entities, the question remains: Should units of the two quantities be known by the same name? The author would answer this question in the negative. It is always awkward, and tends to confusion, when the same name is used for units of two physically different quantities. One will not be certain in all cases which quantity he is dealing with. A number of examples of this sort of confusion are readily found. An instance is the "pound," used for the unit of mass and also for the unit of force or weight in engineering. This use of "pound" as the name for both units tends to obscure the difference between mass and weight, and to complicate discussions of the variation of weight arising from the variation of the acceleration of gravity. Another example occurs in connection with the units of energy and torque. The term "kilogram-meter" might serve for the unit of either energy or torque. In order to show which is meant, however, it is considered[6] worth while, when giving the unit of torque, to reverse the customary designation of the unit of energy, thus using "meter-kilogram" for the torque unit; or, following Kennelly, to indicate that it is a perpendicular product by the expression "kilogram perp. meter."

---

[6] C. Hering, Conversion Tables, p. 72; 1904.

Nomenclature is sometimes proposed which overlooks the disadvantage of calling two different things by the same name. Thus, in the Giorgi system of units described below, it was proposed to call the unit of magnetic permeance the henry. This suggestion has not met with much favor; while permeance has the same dimensional formula as inductance, it is none the less a distinct physical quantity. The same fundamental objection applies to a proposal now being considered[7] to call a unit of luminous flux the watt. Luminous flux is detected physiologically, and as long as it has a physiological aspect can not be expressed in terms of a purely physical unit.

Still another similar case is the use of "centimeter" as the name for the cgs electrostatic unit of capacity and also as the name for the cgs electromagnetic unit of inductance. Neither inductance nor capacity, of course, is physically the same as length and the name is therefore not entirely satisfactory.

Finally, the objection to using the same name for units of two or more different physical quantities may be put upon the basis of convenience. It conduces to misunderstandings to use a word in several different meanings. The difficulties are perhaps less serious after one becomes familiar with the nomenclature and understands the double meanings, but they are a serious stumblingblock to the formation of ideas by students. In practice it is better to have the units distinctively named. So long as "gauss" is used both for the unit of B and of H, if one were told that 100 gausses were used in the iron of a certain apparatus (similarly to the use of a certain number of amperes or volts in an electric circuit) he would not know unless aided by context or convention whether gausses of B or of H were meant. The difficulty is made worse by the fact that the name "gauss" has been used for the unit of still another quantity; it was tentatively adopted by the British association committee on electrical standards in 1895 for the cgs unit of magnetomotive force.

At the present time gauss is used more generally for the cgs unit of B than in any other sense,[8] and it is probably well to use it only in that way. A name that is widely used for the cgs unit of H is the gilbert per centimeter, the cgs unit of $\mathfrak{F}$ being the gilbert. (This is similar to the expression of electric field intensity in volts per centimeter.) The cgs unit of ϕ is the maxwell. When it is desired to avoid the term "gauss" altogether, the cgs unit of B is called the maxwell per square centimeter.

---

[7] Ives, Phys. Rev., 5, p. 270; 1915.

[8] The statement is frequently made that the cgs unit of H is regularly called the "gauss" in terrestrial magnetic work. This is by no means true, there being no consistency of practice regarding the unit of H in that field of work.

IV. RATIONALIZATION OF THE UNITS

Oliver Heaviside[9] pointed out in 1882 that the factor 4π could be removed from many of the electric and magnetic equations by the use of a new set of units. He called them "rational" units, because some of the equations appeared to have a more reasonable correspondence with the underlying theory when 4π was eliminated. Since that time there have been other proposals to define units which would change the position of 4π in the equations. The term "rationalization" has persisted in the literature, meaning a redistribution of the 4π's in an advantageous manner.

1. THE HEAVISIDE SYSTEM

The units used by Heaviside and by a few recent writers differ by powers of 4π from the ordinary cgs units. In these units the factor 4π is eliminated from certain formulas, and the electric and magnetic equations are made symmetrical. These units are used as a Gaussian system; that is, electrostatic units are used for purely electric quantities and electromagnetic units for magnetic quantities. Every equation containing both electric and magnetic quantities must contain as a factor the first or second power of c, the number of electrostatic units in one electromagnetic unit of electric charge, which is equal to the velocity of light in space. For instance, the equations for magnetic flux become

$$\phi = c\frac{\mathfrak{L}I}{N} = c\int E\,dt$$

Heaviside suggested that units of more practical magnitude could be obtained by taking 10^8 times certain of his units instead of using the various multiples, 10^9, 10^8, 10^{-1}, of the "practical" electromagnetic units. His suggested multiples have never come into use.

---

[9] Electrician, 10, p. 6, 1882; Electrical Papers, 1, pp. 199, 262, 432; 2, pp. 543, 575, 1892.

TABLE 3

Heaviside System

Quantity	Cgs electrostatic units in one Heaviside unit	Equations which lose 4π	Equations which gain 4π
R	4π		
I	$\frac{1}{\sqrt{4\pi}}$		
E	$\sqrt{4\pi}$		$V=\frac{Q}{4\pi Kr}$
Q	$\frac{1}{\sqrt{4\pi}}$		$F=\frac{QQ'}{4\pi Kr^2}$
C	$\frac{1}{4\pi}$	$C=\frac{KS}{l}$	
K	1		
$\mathcal{E}$	$\sqrt{4\pi}$		$\mathcal{E}=\frac{Q}{4\pi Kr^2}$
D	$\frac{1}{\sqrt{4\pi}}$	$D=K\mathcal{E}$	
$\mathcal{L}$[a]	4π	$\mathcal{L}=\mu N^2 L.f\left(\frac{L}{L_1}\right)$	

Quantity	Cgs electromagnetic units in one Heaviside unit	Equations which lose 4π	Equations which gain 4π
$\mathfrak{F}$	$\sqrt{4\pi}$	$\mathfrak{F}=\frac{1}{c}NI$	$\Omega=\frac{m}{4\pi\mu r}$
H	$\sqrt{4\pi}$		$H=\frac{m}{4\pi\mu r^2}$
ϕ	$\sqrt{4\pi}$	$\phi=m$	
B	$\sqrt{4\pi}$		
μ	1		
$\mathfrak{R}$	1		
J	$\frac{1}{\sqrt{4\pi}}$	$B=B_0+J$	
κ	$\frac{1}{4\pi}$	$\mu=\mu_0+\kappa$	
m	$\frac{1}{\sqrt{4\pi}}$		$F=\frac{mm'}{4\pi\mu r^2}$

[a] In the formula, L = radius and L_1 = length of a solenoid, and f means "function of."

Table 3 shows that the factor 4π has been removed from every equation which contained it in the ordinary systems. The same factor has been caused to appear in certain equations which were formerly free from it. It is sometimes stated as the main objection against the Heaviside system that it merely shifts the 4π from some formulas to others. However, the existence of 4π in the formulas

$$V = \frac{Q}{4\pi Kr}, F = \frac{QQ'}{4\pi Kr^2}, \text{ and } \mathcal{E} = \frac{Q}{4\pi Kr^2}$$

and the three analogous formuıas in magnetism are not troublesome because these equations are seldom used in numerical computations. The 4π is removed from the equations used in practical work, where its presence is obnoxious. Furthermore there is some theoretical justification for the 4π in those equations which contain it when Heaviside units are used. Consider, for instance, $H = \frac{m}{4\pi\mu r^2}$. If we define the unit pole so that unit flux emanates from it, we should have, since $B = \frac{m}{S}$, for a spherical surface surrounding m at the distance r, $B = \frac{m}{4\pi r^2}$. From $B = \mu H$, it follows that $H = \frac{m}{4\pi\mu r^2}$; that is, $4\pi r^2$ suggests the circumscribing sphere..

The 4π is not only removed from $\mathfrak{F} = 4\pi NI$, but also from curl $H = 4\pi\ U$ and other forms of the First Law of Electromagetism. (The various forms of the law are given on p. 625.) Some forms of the law do not contain 4π in the ordinary units, but do in Heaviside units, as follows:

$$\Omega = I\,\frac{\omega}{4c}\ (\omega = \text{solid angle})$$

$$dH = \frac{Idl}{4\pi cr^2}\sin\,(r, dl)$$

$$H = \frac{I}{2\pi cr}, \text{ for an infinitely long, straight conductor.}$$

Many formulas for electrostatic capacity are more convenient in Heaviside than in ordinary units. The capacity of a sphere, however, is Kr in ordinary units, and $4\pi Kr$ in Heaviside units. It is desirable to have the 4π, which originates in the properties of a sphere, appear in the formulas pertaining to spheres rather than elsewhere. It is a practical convenience, also, to have the awkward numerical coefficient in the formula for a sphere rather than in the formula for a plate condenser, $C=\frac{KS}{l}$, since the latter is the only case that is frequently met with in practice.

In the Heaviside system the factor 4π is not only removed from all the formulas where it occurs in the ordinary systems to more appropriate places in the theory, but the formulas of electrostatics and magnetism are also made identical in form. The symmetry and convenience of the system have aroused admiration in many who have studied the electric units. It was seriously considered for general adoption in England in 1895 and again in 1905. The enormous difficulties of changing the magnitudes of practically all electric units and standards stood in the way and will render the change more and more impossible as time goes on. Some writers[10] on the theory of electricity use these units at the present time, leaving it to their readers to introduce conversion factors when applying the theory to measurements. This makes the reading of their works much more difficult for the majority of students and electrical workers. As already shown, the 4π necessarily appears in some places, so that the reader is not freed from considering it but must deal with it in a way entirely unfamiliar to him. The removal of this factor from certain equations is furthermore not necessarily an advantage, as will be shown below (p. 626).

2. OTHER ATTEMPTS TO ELIMINATE 4π

The demand for a rationalization of the units has increased as electric waves have come into prominence, requiring the simultaneous use of more parts of electromagnetic theory than other phenomena require. In 1900 the American Institute of Electrical Engineers adopted a recommendation to bring up the matter at the next international electrical congress.

There have been a number of attempts to evade the 4π difficulty without recourse to the Heaviside system, which would require such an uprooting of all existing units and standards in electricity. The first proposal was that of Prof. John Perry in 1889, and all the subsequent proposals have been variations of Perry's. He was requested by the British association electrical standards committee to prepare a report on magnetic units and published his proposal [11] in 1891. The idea was to define a new unit of permeability so as to make $\mu_0 = 4\pi \times 10^{-9}$. The unit of $\mathfrak{F}$ was to be the ampere-turn, of H the ampere-turn per centimeter, and of ϕ and B 10^8 times the cgs electromagnetic units. These units permitted the retaining of the equation $B = \mu H$, unchanged in form. They also gave the following simplified equations:

---

[10] H. A. Lorentz, The Theory of Electrons, 1909; O. W. Richardson, The Electron Theory of Matter, 1914.

$$\mathfrak{F} = NI \text{ (} I \text{ being in amperes).}$$

$$\frac{d\phi}{dt} = E \text{ (volts).}$$

The 4π is eliminated from the first of these equations and the factor 10^8 from the second. These units do not furnish a satisfactory solution to the difficulty because of the change in the value of μ. The convenience of having $\mu = 1$ for the ether or for air has been too great to be sacrificed.

Since Perry's proposal, the same or nearly the same idea has been suggested by several different persons. F. G. Baily [12] made the identical suggestion in 1895. In 1900 R. A. Fessenden [13] proposed that μ_0 be taken $= 4\pi$, and that similarly a new unit for dielectric constant be defined such that $K_0 = \frac{1}{4\pi}$. The unit of ϕ was to be the cgs electromagnetic unit, and the unit of $\mathfrak{F}$ 10 ampere-turns. This proposal redistributed the 4π's in the electric and magnetic equations just as the Heaviside units do. Objections to giving μ_0 and K_0 values different from 1 has prevented acceptance of this system, just as in the case of the Perry units.

The system proposed by Fessenden involved the abandonment of the ohm, ampere, and other "practical" units and the use of cgs electromagnetic units instead. A modification of Fessenden's system was suggested by J. A. Fleming.[14] The value of μ_0 was taken $= 4\pi$, as in Fessenden's system, and the "practical" multiples of the cgs units suggested by Heaviside were used; that is, the unit of resistance was to be 10^8 cgs electromagnetic units, the unit of current 1 cgs unit, etc. The single multiplier 10^8 was to be used. The advantage of these proposed units is slight compared with the inconvenience of abandoning those at present in use.

---

[11] Electrician, 27, p. 355; 1891.

[12] Electrician, 35, p. 449; 1895.

[13] Elec. World, 35, p. 282, 1900; Phys. Rev., 10, pp. 1, 83, 1900.

[14] Electrician, 44, pp. 324, 366, 402; 1900.

It was shown by G. Giorgi[15] in 1901 that an entire system could be built up about the idea of Perry retaining the ordinary units such as the ohm and the volt. The same system was proposed a little later by D. Robertson. Giorgi called it the "absolute practical" system, because it is a single coherent system utilizing the "practical" electric units. The system has a unique dimensional basis, the fundamental quantities being length, mass, time, and electric resistance. As the units of these he chose the meter, the kilogram, the second, and the international ohm. This system is rationalized—that is, the 4 π's are redistributed—exactly as in the Heaviside and the Fessenden systems. There is a very complete correspondence of the electric and magnetic equations. Because of the symmetry and consistency of the system, Giorgi was led to give the same name to units having the same dimensions; for example, henry for inductance and for permeance, ampere for current and for magnetomotive force. He would also express both energy and torque in joules. Such terminology is misleading, as pointed out above; ampere-turn is a much better name for the unit of magnetomotive force, reserving ampere for current.

Many of the units are those at present in use. A few, like the coulomb per square meter and the ampere-turn per meter, are not used. The weber is not used, being too large a unit for the requirements of practice. The units of K and μ are, of course, the least satisfactory. They are so chosen that $K_0 = 8.842 \times 10^{-12}$ and $\mu_0 = 1.2566 \times 10^{-6}$. The Heaviside system is preferable in this respect, since it makes $K_0 = 1$ and $\mu_0 = 1$. The superiority of the Giorgi system is its retention of the ordinary "practical" units for the principal electric quantities. Its equations also are slightly more simple in form than the Heaviside equations, since the factor c is not required in $\mathfrak{F} = NI$ and other equations involving both electric and magnetic quantities. In its completeness and consistency the Giorgi system is admirable. Its advantages, however, largely depend on acceptance of the system as a whole, and the requirements of practice always work against the consistent use of a single system of units. In practice, convenient decimal multiples are used.

---

[15] Electrician, 49, p. 223, 1902; Trans. Int. Cong., St. Louis, 1904, 1, pp. 130, 136.

TABLE 4

Giorgi System

Quantity	Unit	Dimensional formula	Cgs electromagnetic units in one Giorgi unit
R	Ohm	$[R]$	10^9
I	Ampere	$\left[\frac{LM^{1/2}}{T^{3/2}R^{1/2}}\right]$	10^{-1}
E	Volt	$\left[\frac{LM^{1/2}R^{1/2}}{T^{3/2}}\right]$	10^8
Q	Coulomb	$\left[\frac{LM^{1/2}}{T^{1/2}R^{1/2}}\right]$	10^{-1}
C	Farad	$\left[\frac{T}{R}\right]$	10^{-9}
K	Farad per meter	$\left[\frac{T}{LR}\right]$	$\frac{4\pi}{10^{11}}$
$\mathcal{E}$	Volt per meter	$\left[\frac{M^{1/2}R^{1/2}}{T^{3/2}}\right]$	10^6
D	Coulomb per m²	$\left[\frac{M^{1/2}}{LT^{1/2}R^{1/2}}\right]$	10^{-5}
$\mathcal{L}$	Henry	$[TR]$	10^9
$\mathfrak{F}$	Ampere	$\left[\frac{LM^{1/2}}{T^{3/2}R^{1/2}}\right]$	$\frac{4\pi}{10}$
H	Ampere per meter	$\left[\frac{M^{1/2}}{T^{3/2}R^{1/2}}\right]$	$\frac{4\pi}{10^3}$
ϕ	Weber	$\left[\frac{LM^{1/2}R^{1/2}}{T^{1/2}}\right]$	10^8
B	Weber per m²	$\left[\frac{M^{1/2}R^{1/2}}{LT^{1/2}}\right]$	10^4
μ	Henry per meter	$\left[\frac{TR}{L}\right]$	$\frac{10^7}{4\pi}$
$\mathfrak{R}$	1/henry	$\left[\frac{1}{TR}\right]$	$\frac{4\pi}{10^9}$
J	Weber per m²	$\left[\frac{M^{1/2}R^{1/2}}{LT^{1/2}}\right]$	$\frac{10^4}{4\pi}$
κ	Henry per meter	$\left[\frac{TR}{L}\right]$	$\frac{10^7}{(4\pi)^2}$
m	Weber	$\left[\frac{LM^{1/2}R^{1/2}}{T^{1/2}}\right]$	$\frac{10^8}{4\pi}$

M. Ascoli has recently shown[16] that it is possible to frame a system which retains the ordinary "practical" units for certain quantities, but is based on the meter, kilogram, second, and $\mu_0 = 1$;

---

[16] L'Elettrotecnica, **2**, p. 731, 1915. (Translation by Kennelly in Elec. World, **67**, p. 876, 1916.)

by inserting a numerical factor λ in the equation $F=\frac{2mI}{\lambda l}$ (F is the force on a magnetic pole m at distance l from the infinitely long, straight current I). He states that this quantity λ is a fifth fundamental quantity in a system of electric and magnetic units. This does not seem justified, for λ is not a physical quantity or property. It is merely a numerical constant, of the same standing as a constant a would be in the relation between current and quantity of electricity, thus, $I=\frac{Q}{at}$. It does not lead to any useful result to give λ a value different from unity. In the system which Ascoli proposes (not, of course, for practical use), $\lambda=10^{7/2}=3162$. The magnetic units have peculiar magnitudes in this system. The unit of H, for instance, is $\sqrt{10}$ cgs electromagnetic units. Since this system gives new units of incommensurable values and makes certain equations more complicated, there does not seem to be any justification for the unusual assumption on which it is based. This system does not affect the 4π situation at all; it is like all the other systems discussed in this section merely in that it modifies the accepted equations and units.

The only writer at the present time (so far as the author has found) who uses units such that K_0 and μ_0 contain the factor 4π is Prof. V. Karapetoff. He makes use of the international ohm and ampere as fundamental units, uses the ampere-turn for $\mathfrak{F}$ and the cgs units for ϕ and B. In building up the system of units, he removes the factor 4π from certain defining equations, resulting in new units of K and μ. The relation of these units to 4π is regarded by Prof. Karapetoff as purely an incidental or historical matter. This system has a commendable simplicity. It involves few changes from the ordinary units. The 4π's, of course, require caution, as their removal from certain equations means their reappearance in certain others. This system gives the most logical basis for magnetic units of the Perry type (μ_0 and K_0 different from unity), in that it takes the international ohm and ampere as starting-points in the system instead of μ or K.

All of these proposals to eliminate 4π without recourse to the Heaviside system have involved the incorporation of 4π in the value of μ. The fundamental features of the various systems are compared in the following table:

TABLE 5

Proposals Regarding Magnetic Units

Author of proposal	μ_0	Unit of magnetomotive force	Unit of flux	Remarks
Perry	$4\pi \times 10^{-9}$	Ampere-turn	10^8 cgs electromagnetic	
Fessenden	4π	10 ampere-turns	1 cgs electromagnetic	$K_0 = \frac{1}{4\pi}$ electrostatic. Cgs system rationalized.
Fleming	4π	do	do	Unit of $R = 10^9$ cgs. Unit of $I = 1$ cgs.
Giorgi	$4\pi \times 10^{-7}$	Ampere-turn	10^8 cgs electromagnetic	$K_0 = 8.842 \times 10^{-12}$ electrostatic. "Practical" system rationalized.
Karapetoff[a]	$\frac{4\pi}{10}$	do	1 cgs electromagnetic	$K_0 = \frac{1}{4\pi}$ electrostatic.

[a] The values of μ_0 and K_0 are not fundamental, but derived, in the Karapetoff system. They result from the use of the ampere and ohm as fundamental units together with the elimination of 4π from certain equations.

3. THE TWO SETS OF MAGNETIC UNITS

As pointed out at the beginning of Section III, two sets of magnetic units are actually in use, both being derived from the international electric units. The point of departure between the two is magnetomotive force, the unit being the gilbert in one set of units and the ampere-turn in the other. The ampere-turn is in widespread use, particularly among those who work with magnetic apparatus. It has usually been regarded as an isolated unit rather than a member of a system. It will be shown here that its use leads very simply to a complete set of magnetic units, which are furthermore rationalized at least as satisfactorily as the Heaviside units.

The ampere-turn is a very convenient unit of mmf, the mmf in a magnetic circuit being equal to the product of the number of amperes by the number of turns of the electric circuit linking the magnetic circuit. The magnetic potential difference along a part of the magnetic circuit can be expressed in ampere-turns also, just as volts can be used to express the electric potential difference between two parts of a circuit as well as the total emf induced in the circuit. The ampere-turn is equal to $\frac{4\pi}{10}$ gilberts, and both may be used for mmf's or for mpd's produced otherwise than by electric currents, just as the "pound" is used as a unit for forces produced otherwise than by gravity.

From the ampere-turn is derived the ampere-turn per centimeter as the unit of H. This is a very useful unit, but the name "ampere-turn per centimeter" may be misleading; a new name would be desirable. H inside a solenoid is not equal to the product of the number of amperes by the number of turns per centimeter of winding, except in the case of a torus or a very long, single-layer solenoid. The "per centimeter" in the name of this unit does not apply to "turn" but to "ampere-turn"; that is, in a magnetic circuit, H at any point is the magnetomotive force per unit distance along the magnetic circuit at that point. The unit of mmf being the ampere-turn, the unit of H is thus the ampere-turn per centimeter of the magnetic circuit. Prof. Karapetoff has suggested the name "atcen" as a convenient abbreviation for ampere-turn per centimeter. A possible objection to this term is that its formation suggests a product (as in such words as foot-pound) instead of a quotient, which the "per" indicates. It has, however, the advantage of brevity, and is readily understood.

Table 6 gives the two sets of magnetic units. The relations involving the ampere-turn are here extended to form a complete

TABLE 6

The Two Sets of Magnetic Units

Quantity	Ordinary magnetic units		Ampere-turn units		Ordinary units in one ampere-turn unit
	Unit	Equations	Unit	Equations	
$\mathfrak{F}$	Gilbert	$\mathfrak{F}=\frac{4\pi}{10}NI$	Ampere-turn	$\mathfrak{F}=NI$	$\frac{4\pi}{10}$
H	Gilbert per cm.	$H=\frac{d\mathfrak{F}}{ds}$	Ampere-turn per cm	$H=\frac{d\mathfrak{F}}{ds}$	$\frac{4\pi}{10}$
ϕ	Maxwell	$\phi=10^8\int Edt$	Maxwell	$\phi=10^8\int Edt$	1
B	Maxwell per cm² Gauss	$B=\frac{d\phi}{dS}$	Maxwell per cm² Gauss	$B=\frac{d\phi}{dS}$	1
μ		$B=\mu H$		$B=\frac{4\pi}{10}\mu H$	1
$\mathcal{R}$	Oersted	$\mathcal{R}=\frac{\mathfrak{F}}{\phi}$	Ampere-turn per maxwell	$\mathcal{R}=\frac{\mathfrak{F}}{\phi}$	$\frac{4\pi}{10}$
		$\mathcal{R}=\frac{l}{\mu S}$		$\mathcal{R}=\frac{10l}{4\pi\mu S}$	
J		$B=B_0+4\pi J$	Maxwell per cm²	$B=B_0+J$	$\frac{1}{4\pi}$
κ		$J=\kappa H$		$J=\frac{4\pi}{10}\kappa H$	$\frac{1}{4\pi}$
m		$\mu=\mu_0+4\pi\kappa$ $\phi=4\pi m$ $J=\frac{m}{S}$	Maxwell	$\mu=\mu_0+\kappa$ $\phi=m$ $J=\frac{m}{S}$	$\frac{1}{4\pi}$

system, alternative to the ordinary magnetic units. The table is a supplement to Table 1; the equations are based on the four fundamental units, the international ohm, international ampere, centimeter, and second. In addition to these magnetic units, a few isolated units are also in use, employing the inch instead of the centimeter.

4. THE AMPERE-TURN UNITS

The units of the second set in Table 6 are similar to those of Perry, Fessenden, and Karapetoff, with the very important difference that $\mu_0 = 1$, and thus no new or strange units are introduced. The only novelty is the presentation of the equations required to make the ampere-turn fit in with the units of other magnetic quantities. It fortunately turns out that these equations contain the factor 4π in appropriate places. In a sense, the system is more conveniently "rationalized" than the Heaviside system.

The use of the same unit for magnetic pole strength and for flux is not common, because the two quantities are not equal numerically in the ordinary units. It has, however, been suggested by the authors of systems in which the units are rationalized, as the two quantities have the same physical nature. In analogous fashion, dielectric displacement and electric charge density are physically similar, and the same unit is used for both. The use of the maxwell as the unit of m leads to the important consequence that J is expressed in the same unit as the physically similar B. This usage results in changing the equation $B = B_0 + 4\pi J$ into the simpler $B = B_0 + J$. Some of the equations are thus simplified, not by introducing new units, but by using the ordinary units for quantities to which they have not commonly been applied.

In the ampere-turn units of Table 6 the 4π has been removed from every equation which contained it when using ordinary units. It will also be noted that in the equations given in ampere-turn units 4π occurs only in the factor $\frac{4\pi}{10}$ in connection with μ or κ. This factor in $B = \frac{4\pi}{10}\mu H$ does not mean an addition of 4π to calculations; it merely comes to the surface in this equation because H is expressed in ampere turns, which removes the $\frac{4\pi}{10}$ from the relation between $\mathfrak{F}$ and I. When the field is due to a solenoid, the 4π can not be escaped in the calculations. That it is legitimate in every way to have 4π in the relation between B and H is suggested by the analogous relation in electrostatics, $D=\frac{1}{4\pi}K\mathcal{E}$. Similarly, the equation for permeance, the reciprocal of reluctance, $\frac{1}{\mathcal{R}}=\frac{4\pi}{10}\frac{\mu S}{l}$, is analogous to the equation for capacity of a plate condenser, $C=\frac{1}{4\pi}\frac{KS}{l}$. The fact that 4π appears in the numerator in the magnetic relations and in the denominator in the electrostatic relations is of no physical significance, but explains the appearance of the factor $(4\pi)^2$ in the equations below, pertaining to magnetic poles. The equations on the left are in ordinary magnetic units and on the right in ampere-turn units.

$$\begin{array}{l|l}
\Omega=\dfrac{m}{\mu r} & \Omega=\dfrac{10}{(4\pi)^2}\dfrac{m}{\mu r} \\[2ex]
\Omega=10^7\dfrac{W}{m}\ (W \text{ in joules}) & \Omega=10^8\dfrac{W}{m}\ (W \text{ in joules}) \\[2ex]
H=\dfrac{m}{\mu r^2} & H=\dfrac{10}{(4\pi)^2}\dfrac{m}{\mu r^2} \\[2ex]
mH=F\ (F \text{ in dynes}) & mH=10\,F\ (F \text{ in dynes}) \\[2ex]
F=\dfrac{mm'}{\mu r^2} & F=\dfrac{1}{(4\pi)^2}\dfrac{mm'}{\mu r^2}
\end{array}$$

The awkward factors on the right are not a source of inconvenience in calculations because these equations are of no technical importance whatever. These equations are not even essential to the theoretical development of the international system, as shown in Table 1. In the Heaviside and all other rationalized systems the 4π is removed from equations used in practice and relegated to these equations. In fact, the factor $(4\pi)^2$ really occurs in the Giorgi and similar systems just as it does here, although it does not appear so because one 4π is incorporated in the value of μ. Those systems also possess an apparent superiority over the ampere-turn system in eliminating the 4π from some of the equations for calculating inductance and capacity. This apparent advantage is illusory, since the 4π is in those systems existent in the numerical values of μ and of K, and so numerical calculations would have to deal with it. In the present system μ and K preserve their ordinary values, and $\frac{4\pi}{10}$ accompanies μ in the formal equations.

The removal of 4π from the first equation of Table 6 is of particular importance, as the same change applies to other forms of the same law. This is the first law of electromagnetism, and gives the mathematical relation between electric current and the magnetic field associated with it. Each of the forms given below is used by some writers as the expression of the essential electromagnetic relation. The equations on the left are in the ordinary magnetic units and those on the right in ampere-turn units. In the latter units 4π has been removed from every equation which contained it in ordinary units and has been put into certain others.

$\mathfrak{F}=\frac{4\pi}{10}NI$	$\mathfrak{F}=NI$
$\Omega=\frac{I\omega}{10}$ (ω = solid angle).	$\Omega=\frac{I\omega}{4\pi}$
$\int_s^s Hds=\frac{4\pi}{10}I$ (Integration is once completely around the current.)	$\int_s^s Hds=I$
curl $H=\frac{4\pi}{10}U$	curl $H=U$
$\frac{\sigma}{\mu}=\frac{I}{10}$	$\frac{\sigma}{\mu}=\frac{4\pi}{10}I$
$dH=\frac{I}{10}\frac{dl}{r^2}\sin(r, dl)$	$dH=\frac{I}{4\pi}\frac{dl}{r^2}\sin(r, dl)$
$H=\frac{4\pi}{10}\frac{NI}{L}$, inside an infinitely long solenoid.	$H=\frac{NI}{L}$
$H=\frac{2\pi}{10}\frac{NI}{r}$, at center of a circle of radius r with N turns.	$H=\frac{NI}{2r}$
$H=\frac{2I}{10r}$, for an infinitely long straight conductor.	$H=\frac{I}{2\pi r}$
$F=\frac{1}{10}[Il\times B]$	$F=\frac{1}{10}[Il\times B]$
$\phi=10^8\frac{\mathcal{L}I}{N}$	$\phi=10^8\frac{\mathcal{L}I}{N}$

Perhaps the most striking difference between this and previous systems of units is the shift of 4π in the equations

$$B=\frac{4\pi}{10}\mu H \tag{1}$$

$$\phi=m \tag{2}$$

These equations are thus made more exactly analogous to the electric equations

$$D=\frac{1}{4\pi}K\mathcal{E} \tag{3}$$

$$\iint D dS=Q \tag{4}$$

It is perfectly legitimate and indeed preferable to have the 4π in the first equation of each pair, B and H being physically different quantities (likewise D and $\mathcal{E}$); and to have it removed from the second equation of each pair since the quantities on both sides of the equation are physically similar. Thus, B and H are not numerically equal in nonmagnetic media, and there is little tendency to regard them as physically the same quantity and measurable in the same unit. There is not much likelihood that a single name will be used to mean both maxwell per square centimeter and ampere-turn per centimeter, as "gauss" has been used for the ordinary units of B and H. The 4π in the relation between D and $\mathcal{E}$ has similarly assisted in preventing confusion over their physical nature.

In Heaviside units the 4π is removed from all the equations (1) to (4). This makes electric displacement in a vacuum numerically equal to electric field intensity. These two quantities may then be confused in their physical meanings, precisely as magnetic induction and magnetizing force have become confused as a result of their numerical equality in ordinary units. It is, of course, legitimate and is mathematically convenient to make two different physical quantities have the same numerical value, but it is often misleading and troublesome. It would therefore appear that in the ampere-turn equations the 4π's are more advantageously distributed than in the Heaviside system.

It is interesting to note that in the fourth edition (1911) of his Theorie der Elektrizität, M. Abraham effects a slight rationalization of units by defining a new unit of dielectric displacement by

$$D = K\mathcal{E} \tag{3'}$$

This leads to

$$\iint D dS = 4\pi Q \tag{4'}$$

These are symmetrical with the two magnetic equations in ordinary units:

$$B = \mu H \tag{1'}$$

$$\phi = 4\pi m \tag{2'}$$

The units were defined in this same way by A. G. Webster in his book, The Theory of Electricity and Magnetism (1897). He, however, gave the name "induction" to the quantity defined by $K\mathcal{E}$. According to the view expressed above, these units put the 4π in the least favorable place, both in the electric and the magnetic equations. Abraham mentions as an advantage of these units that they take the 4π out of the usual relation, curl $H = 4\pi \frac{dD}{dt}$, making it

$$\text{curl } H = \frac{dD}{dt},$$

which is thus symmetrical with

$$\text{curl } \mathcal{E} = -\frac{dB}{dt}.$$

This advantage, however, may also be credited to the ampere-turn units.

The characteristics of iron are very commonly shown by means of curves in which the ordinates are B in gausses, and the abscissas are H either in gilberts per centimeter or in ampere-turns per centimeter. A distinction must be observed in interpreting the curves in the two cases. When the abscissas are in gilberts per centimeter, the ratio of ordinate to abscissa for any point on the curve is equal to μ, the permeability. When ampere-turns per centimeter are used, μ is not equal to the ratio of ordinate to abscissa, but is $\frac{10}{4\pi}$ times that ratio.

The information actually wanted for iron is sometimes the ratio of B to B_0 (B_0 being the induction in a nonmagnetic substance with the same H) rather than the ratio of B to H. This would apply to transformer iron, for example. Consequently, magnetic curves may be plotted with both ordinates and abscissas in gausses. The ratio of ordinate to abscissa for any point equals the permeability, entirely independently of any choice of H units. This follows because $\frac{B}{B_0}=\frac{\mu}{\mu_0}$, and $\mu_0=1$.

This discussion of the ampere-turn units is presented purely for the information of those interested in units. It is not intended to suggest that the Bureau will discard the gilbert in favor of the ampere-turn in its own work. Both sets of magnetic units have been found useful, and both will doubtless continue in use.

V. SUMMARY

The electric units ordinarily used are based upon certain standards defined by international congresses. These units may be considered to form a distinct system. They have been called international units to distinguish them from the corresponding units in the electromagnetic system, of which they are the representatives for the purposes of electrical measurements. The international and the electromagnetic units differ by exceedingly small amounts, and the small differences are determined by absolute electrical measurements made from time to time. The international system takes the international ohm, the international ampere, the centimeter, and the second as fundamental units. The unit of magnetic pole strength is relegated to a subordinate position, corresponding with its unimportance in practical work. The dimensional expressions of electric and magnetic units in this system have a simplicity and direct applicability lacking in other systems. The system has, however, no such simplicity or utility in the domain of mechanics nor anywhere except in electricity and magnetism. It in no way tends to supplant the classical system based on length, mass, and time.

Magnetic units have been in a somewhat confused state. The use of the word "gauss" as the name for both the unit of induction and the unit of magnetizing force is one difficulty. The international system furnishes no justification for this double usage. The two quantities have sometimes been looked upon as physically the same. There are reasons, however, for considering them to have an essentially different nature, induction corresponding to the magnetized state of the medium, and magnetizing force being the agency tending to produce that state. The objections to using the same name for units of different physical quantities have been presented. The double use of "gauss" is an inconvenience in practice.

There have been various proposals from time to time to rationalize the electric and magnetic units; that is, to use units such as to redistribute the factor 4π in the equations. In no system is this factor entirely eliminated. The first proposal, that of Heaviside, had much to recommend it and his units are used in some recent theoretical works. However, all the units are different by some power of 4π from the ordinary units, and their general adoption now seems out of the question. Proposals since Heaviside's for the rationalization of the units have involved less change of existing units but have all had the disadvantage of incorporating 4π in the values of the permeability and dielectric constant of empty space.

A very satisfactory rationalization is effected by the use of the ampere-turn as the unit of magnetomotive force, without recourse to any new units. There are two sets of magnetic units in use, based upon the international electric units. In one set the units correspond in magnitude to the ordinary cgs electromagnetic units. In the other, the ampere-turn and derived units are used. The equations required to make the ampere-turn fit in with the units of other magnetic quantities have been given herein. For want of a better name, the units of this set are called ampere-turn units. It has been pointed out that the ampere-turn units are rationalized more nearly like the Heaviside units than any of the systems which have been proposed, in that μ_0 retains its value unity. From one standpoint the 4π's are even better distributed than in the Heaviside system. It is of interest to find that units actually in use constitute a system which is not at all inferior to the various proposed systems. This presentation of the ampere-turn units has been given as a contribution to the discussion of magnetic units, and in no sense as a proposal to discontinue the use of the gilbert and other, more common units.

In conclusion, this study has shown that the international system, based upon and representing the electromagnetic system, is a convenient and satisfactory system of units for the purposes of electric and magnetic measurements. Proposed changes in some or all of the units do not appear to offer advantages such as to justify the confusion and inconvenience of changing the units as ordinarily used.

WASHINGTON, May 22, 1916.

APPENDIX

SYMBOLS USED

B = magnetic induction.
C = electrostatic capacity.
c = velocity of light.
D = electric displacement.
E = electromotive force.
$\mathcal{E}$ = electric field intensity.
F = force.
$\mathfrak{F}$ = magnetomotive force.
H = magnetizing force.
I = current.
J = intensity of magnetization.
K = dielectric constant.
K_0 = dielectric constant of space.
$L = l$ = length.
$\mathcal{L} = L$ = self-inductance.
M = mass.
$\mathcal{M} = M$ = mutual inductance.
m = magnetic pole strength.
N = number of turns.
P = power.
Q = quantity of electricity.
R = resistance.
$\mathcal{R}$ = reluctance.
r = distance from a point.
S = area.
s = length along a path.
$T = t$ = time.
U = current density.
V = electric potential.
W = energy.
Z = impedance.
γ = conductivity.
δ = mass resistivity.
κ = magnetic susceptibility.
μ = permeability.
μ_0 = permeability of space.
ρ = volume resistivity.
σ = strength of a magnetic shell.
ϕ = magnetic flux.
Ω = magnetic potential.

THE SACCHARIMETRIC NORMAL WEIGHT AND THE SPECIFIC ROTATION OF DEXTROSE

By Richard F. Jackson

CONTENTS

Page
I. Introduction 633
  1. Preliminary 633
  2. Historical 634
II. Preparation of pure dextrose and of dextrose solutions 636
  1. Purification of dextrose 636
  2. Elimination of moisture 639
  3. Preparation of solutions for polarization 640
  4. Density of dextrose solutions 641
III. Apparatus and temperature control 642
  1. Physical apparatus 642
  2. Temperature corrections 642
  3. Quartz control plates 643
IV. Measurements 644
  1. Determination of the normal weight of dextrose 644
  2. The absolute rotation of the normal solution for wave length 5461 A. 646
  3. Variation of saccharimetric rotation with concentration of solution. 647
  4. The specific rotation for wave length 5461 A and its interpolation formula 651
V. Summary 652

I. INTRODUCTION

1. PRELIMINARY

The polarimetric constants of the sugar group are in but few instances known with certainty. Recently the Bureau of Standards has undertaken to ascertain these values with the requisite precision and has published certain important data upon sucrose. The substance studied in the present paper, namely, dextrose, is important because of its wide distribution in nature and its commercial utility.

The purpose in view in studying dextrose was threefold. First. The purified substance was added to the list of standard samples[1] of this Bureau as a standard reducing sugar, in order to assist in standardizing reducing sugar analysis. It was therefore necessary that the purification and the properties of the substance should receive as thorough a study as is the case with the other standard samples. Second. The normal weight required to be determined in order that the quartz-wedge saccharimeter might become available in analyzing the substance. Third. Its rotation of monochromatic light required further study. Bates[2] has shown that the yellow-green line of the mercury spectrum ($\lambda = 5461$ A) possesses many advantages over the D lines of sodium light, and consequently this Bureau has advocated expressing rotation in terms of this wave length.

---

[1] Bureau of Standards Circular No. 25.

2. HISTORICAL

Previous to 1876 a number of determinations were made of the specific rotation of dextrose before it was realized that the values obtained were functions of the concentration of the solution. In 1876 Tollens[3] systematically studied the rotation and discovered the considerable variation with concentration. From his data he prepared an interpolation formula in terms of dextrose hydrate.

In 1884 he[4] extended his measurements over the entire range of concentrations and recalculated his previous formula in terms of anhydrous dextrose. He expressed his first measurements by the formula $\left[\alpha\right]_D^{20.0} = 52.71795 + 0.018796p + 0.00051683p^2$, where p is per cent of anhydrous dextrose. The second series of measurements revealed apparently an error of about a quarter of a degree in the formula, and this amount was consequently deducted from the constant term. The resulting figure was then rounded off to 52.50, leaving the interpolation formula

$$\left[\alpha\right]_D^{20.0} = 52.50 + 0.018796p + 0.00051683p^2.$$

Since this measurement no systematic study has been made of the rotation of dextrose.

The very divergent values which have been suggested for the normal weight are summed up by Browne.[5] The entire range, including Browne's own computation, extends from 32.25 g to 32.82 g, the extreme variation being about 2 per cent. The suggested value of the normal weight has in each instance been obtained by computation.

Landolt[6] calculated from Tollens' specific rotation data the formula $p = 0.948\alpha - 0.0032\alpha^2$, where p is per cent dextrose and α the rotation of the D lines for a 200-mm tube. He then found by direct determination that the relation between the rotation on the saccharimeter with white light and the monochromatic rotation was expressed by the formula $1°V = 0.3448 \pm 0.0008$ circular degrees (sodium light). He then substituted the value 34.48 for a in his formula and obtained 28.88 per cent as the concentration of the solution which would rotate 100°*V* on the saccharimeter. If 28.88 is substituted for p in Tollens' formula, we find 53°473 for the specific rotation of the normal solution. Such a solution contains 32.65 g dextrose, which is thus the normal weight suggested. Inasmuch as the specific rotation varies with concentration, he proposed a different normal weight for each concentration, a preliminary assay being necessary to determine the approximate concentration.

---

[2] This Bulletin, 2, p. 239; 1906.

[3] Tollens, Berichte, 9, p. 1531; 1876.

[4] Berichte, 17, p. 2234; 1884.

[5] J. Ind. Eng. Chem., 2, p. 526; 1910.

[6] Optische Drehungsvermögen, p. 447; 1898.

Sidersky[7] assumed for dextrose the same rotary dispersion as for sucrose (although Landolt's previous statement was to the contrary). He selected 52°80 as the specific rotation of the normal solution and calculated the normal weight from the inverse ratio of the specific rotations and the normal weight of sucrose (26.00 g). He found for the normal weight 32.82 g.

From Tollens' equation 52°80 proves to be the specific rotation of a 12.14 per cent solution of dextrose which is very far from the concentration of the normal solution on the basis of the Herzfeld-Schönrock calibration.

Tucker,[8] making similar assumptions but taking the value 53 for the specific rotation of dextrose, found 32.68 g for the normal weight.

Browne[9] performed the calculation more carefully. He recalculated Tollens' formula to the more convenient form $\left[\alpha\right]^{20.0}_{D} = 52.50 + 0.0277\,c + 0.00022\,c^2$ and by successive approximations found the exact specific rotation of the normal solution. The normal weight was then calculated at first from the inverse ratio of specific rotations of sucrose and dextrose. To correct for the difference in rotation dispersion between sucrose and dextrose, he used Landolt's equation; $1°V = 0°3448$ circular degrees (sodium light) and found for the normal weight 32.248 g in 100 true cubic centimeters. He advised using at all concentrations this uniform normal weight. When the concentration deviates from the normal, the correction due to the change of specific rotation is obtained from a table which he prepared.

---

[7] Polarisation et Saccharimetrie, p. 100; 1908.

[8] Manual of Sugar Analysis, p. 292; 1905.

[9] J. Ind. Eng. Chem., 2, p. 526; 1910.

Browne's calculation is rigorously correct as far as the available data permit. It is, however, based upon experimental values which in themselves are far from certain. Considering the deviation between Tollens' first and second series of experiments and the advances made in polariscopic apparatus in the last 30 years, it seems probable that new data would yield more reliable values.

Landolt's data[10] on the relation between 1 °V and circular degrees of sodium light is also open to question. This value to which Landolt ascribes an uncertainty of ±.0008 was obtained in 1866 upon a saccharimeter illuminated with white light. Since no mention is made of the use of a bichromate solution filter, it is probable that it was not used, especially since the latter did not come into general use until nearly 40 years later. The presence of the light filter would cause a considerable variation in this value.

Recently Bates and Jackson[11] have made a study of the rotation of the normal sucrose solution which is the fundamental standard for the hundred-degree point of the saccharimeter. They found that the existing standard—namely, that established by Herzfeld and Schönrock—was about 0.1 per cent too high. Bates and Jackson by a series of careful determinations found that the conversion factor for $\lambda = 5892.5$ A was $34^\circ620$ and for $\lambda = 5461.$ A $40^\circ690$.

II. PREPARATION OF PURE DEXTROSE AND OF DEXTROSE SOLUTIONS

1. PURIFICATION OF DEXTROSE

The material used for the preparation of pure dextrose was obtained from three sources; crude commercial glucose, Merck's "Highest Purity" dextrose, and an invert sugar solution.

The purest form of commercial glucose which could be obtained was a brownish-colored granular substance which was sold under the trade name of "Cerelose." The crude sugar contained 87.2 per cent dextrose, 3.9 per cent of nonfermentable sugar, 0.55 per cent ash, and a quantity of dextrins.

A large quantity of the glucose was shaken in a shaking machine with aqueous alcohol in order to wash the crystals. It was then poured into a centrifugal machine, drained and again washed. This preliminary treatment removed a portion of the impurities adhering to the surfaces of the crystals and assisted the later operations. The washed substance was then dissolved by slight warming in 40 per cent of its weight of water and 140 cubic centimeters of alcohol added for each 100 g of the substance. The whole mixture was warmed on a steam bath for a short time and was then filtered to remove the precipitated dextrins. The filtrate after cooling was poured into a shaking machine, seeded with a few crystals of dextrose, and agitated continuously until crystallization was complete. This usually required about 48 hours. The crystal mass was poured on the centrifugal machine, drained, and thoroughly washed with alcohol. The crystals from this first operation were fine, well-formed, and perfectly white. Upon resolution for a second crystallization there was in general but a slight trace of the original discoloration.

---

[10] Zs. anal. Chem., **5**, p. 412; 1866.

[11] This Bulletin, **13**, p. 67; 1916.

The second crystallization was from aqueous solution. The crystals were dissolved by warming in distilled water to form a solution of about 60° Brix. The solution was filtered, cooled, and shaken in the crystallizer until crystallization was complete. Crystallization from water is particularly favorable to the formation of pure crystals. They are in every instance small and their rate of formation, which depends partly upon the speed of the reaction β glucose $\rightarrow$ α glucose in the solution, is slow. The crystals accordingly are perfect and free from inclusions.

In the absence of special tests for possible impurities the criterion of purity which was taken was constancy of composition after treatment with varied procedure. It was found that direct recrystallization from water solution soon produced a sample which repeated recrystallizations did not alter even after four or five operations.

Attention was then turned to the mother liquors. These were boiled in vacuo in the boiling apparatus described previously[12] until sufficiently supersaturated to crystallize or were united with crystals of about the same purity and the whole mixture, dissolved, concentrated, and crystallized. This process was carried out systematically in the manner usually followed in fractional crystallizations.[13] To identify the samples the numerical order of the fractions is shown in Fig. 1.

Merck's "Highest Purity" dextrose was white in color and was already fairly pure. It was recrystallized from aqueous solution three times, the mother liquor being rejected after each recrystallization. The final product was designated sample M.

---

[12] This Bulletin, **18**, p. 75; 1916.

[13] This Bulletin, **18**, p. 93; 1916.

For the preparation of the two invert sugar solutions from which other quantities of dextrose were prepared the purest cane sugar of commerce was utilized. One solution was inverted by invertase prepared as recommended by Hudson.[14] The other was inverted by adding a small quantity of hydrochloric acid and allowing it to remain at room temperature for somewhat more than the calculated length of time sufficient to produce 99.9 per cent inversion, after which it was neutralized with sodium hydroxide. Both solutions were then boiled in vacuo until concentrated to a thick sirup. They were then mixed with a large volume of alcohol in the shaking machine and the dextrose allowed to crystallize. At the end of two or three weeks the crystals were separated in the centrifugal machine, washed, and three or four times recrystallized. The crystals from the acid inversion were designated sample H; those from the invertase inversion sample I. Some small pure residues containing portions of both H and I were combined and recrystallized to form sample J. A considerable quantity of pure residues from various sources were combined and twice recrystallized to form sample A. A portion of this was recrystallized, the mother liquor selected and twice crystallized to form sample C.

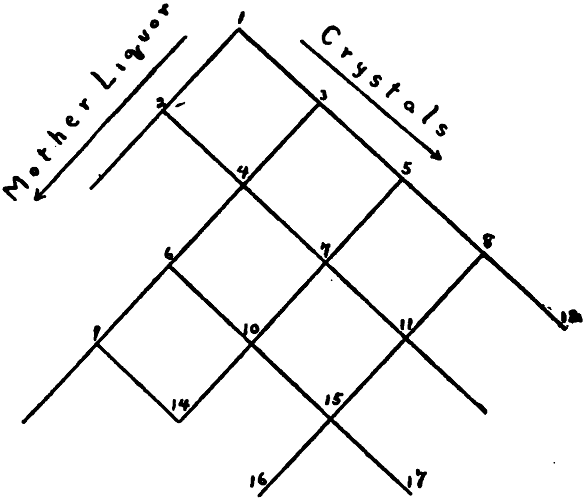


FIG. 1.—*Diagrammatic representation of fractional crystallization*

A portion of sample C was dissolved in a small quantity of pure water and poured into a large quantity of nearly absolute alcohol. The crystals were almost anhydrous and were designated sample E. The accessory materials such as water and alcohol used in these preparations were purified in the usual manner.

---

[14] J. Ind. Eng. Chem., 2, p. 143; 1910.

The probable impurities if such persisted at the completion of the purification of the sugar were of very different nature in the two sets of samples from glucose and from invert sugar. The dextrins which conceivably could contaminate the sample prepared from commercial glucose have a specific rotation of about +198. The levulose which is the only probable impurity in the sample prepared from invert sugar has a specific rotation of about −90. The fact that the materials from the two sources had the same rotary power is strong evidence of the purity of both.

2. ELIMINATION OF MOISTURE

From aqueous solution dextrose separates with one molecule of crystal water. It loses this water at 60° C, leaving the crystals in a thoroughly disintegrated condition. If it is stirred frequently the tendency to cinter together is prevented. Because of this complete disintegration the danger of inclusion of moisture within the crystals seems practically nil. The drying problem then resolves itself into the removal of surface moisture.

The first consideration was the stability of dextrose at high temperatures. Unfortunately in distinction to sucrose[15] no method of detecting minute quantities of caramel exists. The most easily recognized property of caramel, namely, its power to reduce alkaline copper solutions, is entirely masked by the great reducing power of the dextrose itself. However, by leaving equal weights of sucrose and dextrose in an oven at 100° C overnight, it became apparent by the color change that dextrose was more resistant to a high temperature than sucrose. We therefore avoid decomposition of dextrose if we heat at any given temperature for no greater length of time than would cause a negligible caramelization of sucrose.

The sample from which the crystal water had been removed was heated electrically to 60° in a weighing bottle placed in a long glass tube together with a quantity of ignited quicklime. The tube was then exhausted by a Geryk pump to about 0.01 mm, heating and pumping being continued for three or four hours. The bottle remained in the vacuum for two days. It was then removed and weighed. The loss in weight was about 0.02 per cent. Upon repeating the process the first dry weight was found to be constant. In fact, this was the general experience in weighing the samples for the 50 or more determinations of the rotation.

---

[15] This Bulletin, 18, p. 84; 1916.

In order to ascertain whether this constant weight represented the perfectly dry substance, three experiments were tried at higher temperatures. In each case the sample was previously dried to constant weight in the vacuum at 60° C. One sample was then heated under the same conditions to 80° C, the other two to 100° and 125°, respectively. In no case was a further loss of weight discovered. If any considerable surface moisture were present, it would probably have shown some tendency to escape within a temperature interval of 65°.

The procedure for drying the substance in preparation for polarization then was merely to heat at 60° to 70° C in a vacuum of 0.01 mm for three or four hours or until the weight became constant.

3. PREPARATION OF SOLUTIONS FOR POLARIZATION

In order to prepare a solution for polarization the approximate required quantity of dextrose which had been freed of its crystal water was transferred to a weighed volumetric flask and the flask and substance again weighed. The final drying was performed in a long glass tube of 8 cm diameter, one end of which was drawn down and connected with the vacuum pump. The other end was equipped with a ground glass joint which was large enough to permit inserting the volumetric flask. The portion of the tube containing the sample could be heated electrically to the temperature desired. The drying was repeated in every case until a constant weight was obtained.

Enough distilled water was then added to dissolve the dextrose and the solution was freed from most of the dissolved air by boiling at low temperature in a vacuum. The solution was then adjusted accurately to the graduated volume of the flask after immersion in the water of a thermostat at 20°.00 C for a sufficient length of time. It was then dried by a slightly damp cloth and weighed after remaining in the balance case for a half hour.

The volumetric flasks were those used by Bates and Jackson and were described in the paper referred to. For the present work the calibration was performed repeatedly and the volumes found to be essentially identical with those found previously.

As is well known the freshly dissolved dextrose exhibits the phenomenon of mutarotation. The velocity of this reaction follows the usual law of the monomolecular reaction, its constant being fairly well established. Taking Levy's value[16] of the constant at 20.7 C, namely, $\frac{1}{t} \log_{10} \frac{R_\infty - R_0}{R_\infty - R_t} = 0.00662$, we find that the reaction is 99.99 per cent complete in about 10 hours. The procedure followed was to allow the solution to stand overnight at room temperature. The flask was tightly stoppered and evaporation avoided.

---

[16] Zs. physik. Chem., 17, p. 301; 1895.

4. THE DENSITY OF DEXTROSE SOLUTIONS

The data obtained on the concentration of the solutions were sufficient for the calculation of the density of dextrose solutions at 20°.0 C. The determinations at each of the four concentrations were corrected to a uniform per cent dextrose. Each of these groups of determinations were then averaged and a series of five values obtained (see column 2 of Table 1), which were sufficient for a per cent – density equation. The formula was found to be:

$$D\,\frac{20^\circ}{4^\circ} = 0.99840 + 0.003788\,p + 0.00001412\,p^2$$

where p is per cent dextrose by weight in vacuo. The density as computed by this formula may be considered valid to three or four units in the fifth decimal place for values of p between 5 and 30. In column 3 of Table 1 are given the densities as calculated by the formula. Their agreement with the experimental data is shown by the residuals in column 4. In Table 2 the densities are given at 1 per cent intervals between 4 and 30 per cent.

The only previous determination at 20°.0 C is a series made by Tollens[17] incidentally to his measurements of the rotation. For the sake of comparison we may cite his values at 7.60, 10.14, and 17.60 per cent, for which he found densities 1.0282, 1.0383, and 1.0694, respectively. The corresponding densities found in the present investigation are 1.02801, 1.03826, and 1.06945.

TABLE 1

Data on Density of Dextrose Solutions and Comparison with Interpolation Formula

Concentration by weight in vacuo	Density 20°/4° observed	Density 20°/4° calculated from formula	Residuals, col. 3—col. 2
1	2	3	4
Per cent			
6.5	1.02361	1.02362	+0.00001
12.5	1.04799	1.04796	− .00003
18.5	1.07329	1.07331	+ .00002
23.5	1.09524	1.09522	− .00002
28.9	1.11963	1.11966	+ .00003

---

[17] Landolt and Börnstein, Tabellen, p. 79; 1912.

TABLE 2

Density of Dextrose Solutions Calculated by Formula:

$$D \frac{20^\circ}{4^\circ} = 0.99840 + 0.003788\, p + 0.00001412\, p^2$$

Concentration by weight in vacuo	Density $\frac{20^\circ}{4^\circ}$	Concentration by weight in vacuo	Density $\frac{20^\circ}{4^\circ}$	Concentration by weight in vacuo	Density $\frac{20^\circ}{4^\circ}$
Per cent		Per cent		Per cent	
4	1.01378	13	1.05003	22	1.08857
5	1.01769	14	1.05420	23	1.09299
6	1.02164	15	1.05840	24	1.09744
7	1.02561	16	1.06262	25	1.10192
8	1.02961	17	1.06688	26	1.10643
9	1.03364	18	1.07116	27	1.11097
10	1.03769	19	1.07547	28	1.11553
11	1.04178	20	1.07981	29	1.12013
12	1.04589	21	1.08417	30	1.12475

III. APPARATUS AND TEMPERATURE CONTROL

1. PHYSICAL APPARATUS

The polariscopic apparatus which was used for the observations was fully described in the paper by Bates and Jackson.[18] The discussion on pages 97 to 108 is directly applicable to the present paper. The method of taking observations was also similar to that in the earlier work.

2. TEMPERATURE CORRECTIONS

The temperature corrections for the optical apparatus were described by Bates and Jackson [19] and are directly applicable to the present measurements. The temperature coefficient of the dextrose solutions, however, required especial attention. The temperature coefficient of the specific rotation of dextrose solutions has been previously studied over a wide range of temperatures and has been found to be zero. Since in the present work the variations of temperature were very small, it is permissible to accept this result without question. The actual change of rotation with change of temperature, then, would be due entirely to the change in volume of the solution. The expansion of the normal solution was measured in the vicinity of 20° C and found to be 0.00029. This figure was then also the temperature correction factor for the rotation.

---

[18] This Bulletin, **13**, p. 97; 1916.

[19] Loc. cit.

In addition to this the actual temperature coefficient of rotation was measured for a number of solutions. The data obtained were the very small differences between large numbers and consequently a great many were required to offset the errors of observation. The mean of 37 such determinations gave for the coefficient 0.00028. The mean value 0.000285 was used in the computations at the normal concentrations. For the lower rotations the expansion coefficient was taken to be proportional to the concentration of dextrose between pure water which has a coefficient of 0.00021 and the normal dextrose solution 0.000285. The expansion coefficient is probably not strictly linear with concentration but for the present purpose where the entire correction is small the deviations from the linear relation are negligible. The correction to be applied is then proportional to the rotation and to the expansion coefficient.

3. QUARTZ CONTROL PLATES

There was available for the present investigation a set of seven quartz plates, all of excellent quality, optically homogeneous, and nearly plane parallel, which constitute part of a series of primary standards of this Bureau. Their properties, including their rotations in terms of wave lengths 5892.5 A and 5461 A, have been been studied at this Bureau and at the Physikalisch-Technische Reichsanstalt. The results of the thorough study which these plates have received will be stated in a future publication of this Bureau. Their sugar values were found by dividing their monochromatic rotations by the appropriate conversion factors. For the present work the factors determined by Bates and Jackson, namely, 34°620 for $\lambda = 5892.5$ A and 40°690 for $\lambda = 5461$ A, have been used. Until the final value of the conversion factor is generally agreed upon it is considered of more importance that the proposed normal weight of dextrose shall correspond exactly with 26.000 g of sucrose than with the Herzfeld-Schönrock scale, which is now known to be slightly in error.

A further assumption made in regard to the saccharimetric scale is that the scale readings are rigorously proportional to the rotation of quartz. For example, if a quartz plate rotates 17°310 for $\lambda = 5892.5$ A, its sugar value is exactly 50°00. The same conversion factor is thus applicable to all parts of the saccharimeter scale. This is equivalent to the statement that the saccharimeter scale is proportional to the thickness of the compensating quartz.

IV. MEASUREMENTS

1. DETERMINATION OF THE NORMAL WEIGHT OF DEXTROSE

Twelve independent measurements were made to determine the weight of dextrose which dissolved in 100 true cubic centimeters causes a rotation of 100° S on the sugar scale as determined by Bates and Jackson. The data acquired during the measurements are recorded in Table 3. The values of the normal weight obtained are given in column 7 and were calculated in the following way: The concentration of sugar in each experiment was found by dividing the weight of substance (column 3) by the volume of solution (column 5). The concentration was then divided by the rotation of the solution to give a value of the normal weight which would be the true value, provided the specific rotation were precisely constant over the small range of concentrations measured. This is not exactly true, so that a small correction was applied to bring the normal weight to the value which would have been obtained if the solution observed were at the normal concentration. The specific rotation, as will be shown later, is changing at this concentration 0.021 per cent for each sugar degree change in concentration. The calculated value of the normal weight is then 0.021 per cent, or 6.9 mg too low for each sugar degree above 100° S which the observed solution reads. This correction has been applied and the corrected value recorded in column 7. As appears from the table, the true normal weight of dextrose, or that weight of dextrose which produces on the saccharimeter the same rotation as 26.000 g of sucrose, is 32.231 g weighed in air with brass weights.[20]

The value 32.231 is dependent on the assumption that the hundred-degree point of the saccharimeter is defined according to the conversion factor 34°620 for $\lambda = 5892.5$ A and 40°690 for $\lambda = 5461$ A. If some other standard is used the normal weight is determined by the following relation:

$$\text{Normal weight} = \frac{\text{conversion factor}}{34.620} \times 32.231 \ (\lambda = 5892.5 \text{ A})$$

or

$$\text{normal weight} = \frac{\text{conversion factor}}{40.690} \times 32.231 \ (\lambda = 5461 \text{ A}).$$

---

[20] To specify more rigorously, this is the weight in air of density 0.00119, the mean value during the present experiments.

This formula is strictly applicable for small differences in the conversion factor. Here, again, if the change in weight is enough to cause a measurable change in the specific rotation, a correction of 6.9 mg must be applied for each degree sugar or each 0°346 or 0°407, by which the factor chosen exceeds 34°620, or 40°690 for the respective wave lengths. Thus, if the saccharimeter is standardized, as at present, by the Herzfeld-Schönrock factor 34°657, the normal weight of dextrose becomes 32.264 g. In order to avoid confusion it must be noted that the Herzfeld-Schönrock factor is the one in general use at the date of this publication. If the saccharimeter is controlled by quartz plates certified by this Bureau or by the Physikalish-Technische Reichsanstalt, the Herzfeld-Schönrock data have been used and until further notice will continue to be used in determining the sugar value. Consequently, the weight 32.264 must be taken to rotate 100° S. But if the saccharimeter has been standardized by careful observations of 26.000 g of pure sucrose in 100 cc, or if, as is to be hoped, the conversion factor is modified to 34°620 and 40°690, the normal weight of dextrose becomes 32.231.

TABLE 3

Data on the Concentration and Rotation of the Normal Solution

Expt. No.	Designation of sample	Weight of dextrose (air, brass weights)	Weight of solution (air, brass weights)	Volume of solution	Average observed rotation for two saccharimeters	Normal weight	Rotation observed λ=5461A	Rotation of normal solution λ=5461A
1	2	3	4	5	6	7	8	9
		g	g	cc	sugar deg.	g	deg.	deg.
1	Fraction 5	32.5255	112.096	100.166	100.753	32.234	....	....
2	do	32.3283	112.039	100.183	100.114	32.233	....	....
3	Fraction 8	31.8702	....	100.185	....	....	40.362	40.904
4	do	32.4030	111.889	100.005	100.563	32.222	....	....
5	Fraction 15	32.4778	112.103	100.181	100.604	32.228	....	....
6	Fraction 11	41.7989	....	130.063	99.693	32.233	40.780	40.901
7	Sample C	41.9946	145.439	130.032	100.180	32.239	40.978	40.895
8	Fraction 15	42.9000	....	129.997	102.453	32.228	....	....
20	Sample C	32.1525	111.792	99.993	99.748	32.232	40.792	40.894
21	do	30.4514	105.286	94.121	100.377	32.235	41.051	40.893
24	Fraction 8	30.1672	105.180	94.121	99.436	32.230	40.659	40.892
28	Sample H	32.2959	112.033	100.181	100.026	32.229	40.921	40.912
54	Sample I	32.2670	112.027	100.187	99.914	32.234	40.857	40.888
Av.	....	....	....	....	....	32.231	....	40.897

2. THE ABSOLUTE ROTATION OF THE NORMAL SOLUTION FOR WAVE LENGTH 5461 A

The observations on each solution included, when possible, its rotation in circular degrees for the yellow-green mercury line $\lambda = 5461$ A. These readings were made on the same day as the saccharimeter readings, either preceding or following them. The accepted rotation was the mean of the readings of two observers upon two or three polariscope tubes containing portions of the same solution. The practice was to make about six settings of the instrument for each tube and an equal number for the zero point in alternation. Frequent readings of the thermometers in the air bath or in the polariscope tubes were also taken. At frequent intervals one of the standard quartz plates was read in order to ascertain whether the rotations were consistent with previous measurements. Bates and Jackson applied a correction of −0°.004 to the reading of the normal sucrose solution in order that the value should be the mean of the various optical systems used to purify the light source. This correction has also been applied in the present instance to the normal solution and to the more dilute solutions proportionately to the magnitude of the rotation.

The observed rotations are recorded in column 8 of Table 3. These values were transformed to give the rotations of the normal solution by the simple relation:

$$\frac{\text{Normal weight}}{\text{Weight taken in 100 cc}} \times \text{rotation observed.}$$

This gave a value of the normal rotation which depended upon the assumption that the specific rotation was constant over the range of rotations observed. As this was not strictly true, a small correction was applied. It will be shown later (p. 651) that the specific rotation varies 0°.0136, or 0.0214 per cent for each sugar-degree deviation from the normal concentration. Accordingly, a correction of −0.00875 was applied for each sugar degree above 100°.00 S which the solution rotated. This has been applied in order to obtain the corrected values in column 9. The conclusion is that light of wave length 5461 A is rotated 40°.897 by the normal solution at 20°.00. It is evident from a consideration of the data now available that the rotary dispersion curves of quartz and of dextrose deviate considerably from each other. The normal plate which gives on the saccharimeter a rotation identical with the normal dextrose solution rotates wave length 5461 A 40°690, while the dextrose solution rotates it 40°897.

There is thus a difference of 0°2 in the rotation of this wave length when the quartz wedges are set for a photometric match. Although this color is only 4 per cent transmitted by the 6 per cent and 15 mm bichromate cell, the transmission curve [21] of the latter rises abruptly at this point with increasing wave length. We must, then, conclude that the photometric field is considerably heterochromatic and the eye is obliged to match an intensity of one color by a supposedly equal intensity of a slightly different color. For sucrose [22] the normal solution rotates wave length 5461 A 40°763, which, by comparison with quartz 40°690, indicates a much closer agreement of rotary dispersion curves. We should, therefore, expect a lower degree of reproducibility in reading dextrose than sucrose solutions. This proves in some measure to be the case, but in the process of taking the mean of a sufficient number of readings, the differences apparently disappear.

Furthermore, as the observer's experience increases there proves to be a corresponding improvement in reproducibility. Thus, in experiment No. 1 the readings were scattered over a range of 0°26 S; in No. 2 the greatest difference was 0°12 S. In the whole series, exclusive of experiments 1 and 2, the two observers, reading the same solution upon the same instrument, agreed within 0°03 S.

The experiment was tried of doubling the concentration of bichromate solution, but it did not appear to increase the reproducibility of setting. It was then decided to postpone any further work on a suitable light filter until the rotary dispersion curve of dextrose was known with suitable precision.

3. VARIATION OF SACCHARIMETRIC ROTATION WITH CONCENTRATION OF SOLUTION

In addition to the rotation of dextrose at the normal concentration a complete series of measurements was made at each of four other concentrations, namely, 4/5, 3/5, 2/5, and 1/5 normality. At each of these concentrations the measurements were conducted in exactly the same manner as for the normal concentration, the rotations being compared upon two saccharimeters with the readings of the standard quartz plates.

The experimental work at these concentrations is recorded in Tables 4, 5, 6, and 7. An experiment at 80° S. may be taken as an example. About 4/5 the normal weight was weighed in the volumetric flask, dried, weighed, and dissolved in the usual manner, the data being given in columns 3, 4, and 5. Its rotation was measured with all the precautions and with as many settings of the instruments as in the case of the normal solution. The mean of these readings is given in column 6. The rotation of the 4/5 normal solution was computed by the relation

---

[21] Bureau Standards Circular No. 44, Appendix; 1917.

[22] This Bulletin, 13, p. 217; 1916.

$$\frac{\text{Observed rotation}}{\text{Concentration}} \times 4/5 \times 32.231$$

The result of this computation would be true if the specific rotation were constant over the range of the observed rotations. This is not strictly so, and accordingly a small correction obtained in the manner indicated for the normal solution has been applied. The corrected values are given in column 7. The mean of column 7 in Table 4—namely, 79.639—shows the result of a very considerable deviation of specific rotation with change of concentration. If the specific rotation were constant, the 4/5 normal solution would have read 80.000. The measurements illustrate the importance of applying a correction for concentration when the solution deviates from the normal. Although the deviation of specific rotation is progressive as the dilution increases, the correction passes through a maximum. If expressed in percentage of the measured rotation, the correction is linear.

TABLE 4

Data on the Concentration and Rotation of the 4/5 Normal Solution

Expt. No.	Designation of sample	Weight of dextrose (air, brass weights)	Weight of solution (air, brass weights)	Volume of solution	Average observed rotation on two saccharimeters	Rotation of 4/5 normal solution	Rotation observed λ=5461 A	Rotation of 4/5 normal solution λ=5461 A
1	2	3	4	5	6	7	8	9
		g	g	cc	sugar deg.	sugar deg.	deg.	deg.
9	Sample A	33.5756	142.314	130.018	79.755	79.633	....	....
10	do	25.7430	109.607	100.183	79.368	79.647	32.459	32.572
22	Sample I	33.4408	142.259	130.004	79.445	79.639	32.495	32.575
23	Sample C	25.6511	109.622	100.223	79.023	79.623	32.321	32.567
30	Sample M	25.8337	....	100.181	79.646	79.639	32.5825	32.579
40	Sample J	25.5835	109.548	100.181	78.870	79.647	32.270	32.588
52	Fraction 16	25.6668	....	100.184	79.123	79.642	32.354	32.566
Av	....	....	....	....	....	79.639	....	32.5745

TABLE 5

Data on the Concentration and Rotation of the 3/5 Normal Solution

Expt. No.	Designation of sample	Weight of dextrose (air, brass weights)	Weight of solution (air, brass weights)	Volume of solution	Average observed rotation on two saccharimeters	Rotation of 3/5 normal solution	Rotation observed λ=5461 A	Rotation of 3/5 normal solution λ=5461 A
1	2	3	4	5	6	7	8	9
		g	g	cc	sugar deg.	sugar deg.	deg.	deg.
13	Fraction 8	19.4089	107.245	100.181	59.597	59.488	24.371	24.325
14	do	19.5009	107.321	100.223	59.910	59.539	24.486	24.334
17	Sample C	18.7139		94.121	61.173	59.477	25.013	24.320
18	do	20.0355	107.509	100.223	61.524	59.490	25.160	24.328
34	Fraction 17	19.6780	107.344	100.181	60.437	59.490	24.710	24.323
38	Sample I	18.9178	101.014	94.121	61.846	59.475	25.303	24.333
55	Fraction 15	17.6856		90.801	59.912	59.480	24.512	24.335
Av.						59.491		24.328

TABLE 6

Data on the Concentration and Rotation of the 2/5 Normal Solution

Expt. No.	Designation of sample	Weight of dextrose (air, brass weights)	Weight of solution (air, brass weights)	Volume of solution	Average observed rotation on two saccharimeters	Rotation of 2/5 normal solution	Rotation observed λ=5461 A	Rotation of 2/5 normal solution λ=5461 A
1	2	3	4	5	6	7	8	9
		g	g	cc	sugar deg.	sugar deg.	deg.	deg.
11	Sample A	12.8269	104.818	100.223	39.200	39.490	16.032	16.151
15	Fraction 8	17.2069	136.190	130.016	40.558	39.501	16.577	16.145
16	Sample A	13.2657	104.763	100.000	40.623	39.470	16.603	16.132
31	Sample M	12.1053	98.453	94.121	39.372	39.468	16.094	16.133
43	do	12.1226	98.470	94.121	39.456	39.495	16.140	16.156
46	do	12.9342	104.817	100.181	39.529	39.473	16.161	16.138
50	Sample E	12.2315		94.121	39.807	39.488	16.268	16.138
Av.						39.484		16.142

F. P. Phelps very kindly performed a least square adjustment of the straight line representing the percentage deviation of rotation from strict proportionality. In this adjustment the normal weight was taken as the fixed value 32.231 g and the remaining four series weighted in proportion to the magnitude of the rotation.

The corrections to be applied are given for 5° S intervals in Table 8. These quantities are valid for all readings in a 200 mm tube. If the solution is read in a 400 mm tube, the reading is divided by 2 to find the correction. The latter is then multiplied by 2 and applied to the original reading.

TABLE 7

Data on the Concentration and Rotation of the 1/5 Normal Solution

Expt. No.	Designation of sample	Weight of dextrose (air, brass weights)	Weight of solution (air, brass weights)	Volume of solution	Average observed rotation on two saccharimeters	Rotation of 1/5 normal solution	Rotation observed λ=5461 A	Rotation of 1/5 normal solution λ=5461 A
1	2	3	4	5	6	7	8	9
		g	g	cc	sugar deg.	sugar deg.	deg.	deg.
19	Sample C	6.8326	102.503	100.181	20.813	19.666	8.506	8.038
26	Fraction 8	6.7750	102.523	100.223	20.631	19.670	8.442	8.049
33	Fraction 17	6.8384	102.550	100.223	20.823	19.668	8.518	8.045
37	Sample I	6.6511	102.440	100.181	20.235	19.644	8.292	8.050
41	do	6.9544	102.551	100.181	21.144	19.628	8.658	8.038
49	Sample D	8.6443	132.936	130.000	20.230	19.609	8.287	8.032
53	Sample E	6.0056	92.251	90.214	20.291	19.645		
Av.						19.647		8.042

As has been stated, Browne computed a similar table by using Tollens' data on the specific rotation. Browne's table gives very similar values at the higher values of the rotation, but it deviates from the present direct determination at the lower rotations. For example, the corrections at 80° S, 40° S, and 20° S are according to Browne's computation +.035, +0.48, and +0.30, respectively, The corresponding corrections from the present work are +0.35, +0.53, and +0.35. The deviation seems to cast some doubt upon the second order correction of the specific rotation formula of Tollens from which Browne's data were computed.

TABLE 8

Corrections to be Applied to Saccharimetric Readings of Dextrose Solutions

Scale reading	Correction to be added	Scale reading	Correction to be added	Scale reading	Correction to be added
100	0	65	0.50	30	0.46
95	0.10	60	0.52_6	25	0.41
90	0.20	55	0.54	20	0.35
85	0.28	50	0.55	15	0.28
80	0.35	45	0.54	10	0.20
75	0.41	40	0.53	5	0.10
70	0.46	35	0.50	2	0.05

4. THE SPECIFIC ROTATION OF DEXTROSE FOR WAVE LENGTH 5461 A AND ITS INTERPOLATION FORMULA

In columns 8 of Tables 4, 5, 6, and 7 are given the absolute rotations of the solutions at each of the four concentrations less than normal for the wave length 5461 A. The readings were as numerous and as carefully observed in each experiment as in the case of the normal solution. The accepted mean was converted into the rotation of the n/5 normal solution by the simple arithmetical proportion and application of the correction for the change of specific rotation when the concentration differed from the normality desired. These corrected values are recorded in columns 9 of Tables 4, 5, 6, and 7.

The mean monochromatic rotations for the five concentrations are collected in Table 9 and the values converted into specific rotations by the formula

$$\left[\alpha\right]^{20.0}_{5461\text{A}} = \frac{\alpha \times 100.00}{2 \times \text{weight dextrose in vacuo}}$$

In calculating the atmospheric buoyancy correction the mean value of the density of anhydrous dextrose was taken to be 1.54. This is the rounded-off mean of three values reported,[23] namely, those of Pionchon (1.538), Bödecker (1.5384), and Schoorl (1.544). The density of the air in the balance case was computed from its temperature and the barometric pressure.

TABLE 9

Summary of Data on Monochromatic Rotations of Dextrose Solutions

Normality of solution	Vacuum weight of dextrose in 100 cc	Rotation observed $\lambda = 5461$ A	Rotation calculated from formula	$\left[\alpha\right]^{20.0}_{5461\text{A}}$ calculated from formula
1	2	3	4	5
	g	deg.	deg.	deg.
N	32.2515	40.897	40.898	63.404
4/5 N	25.801	32.574_5	32.576	63.129
3/5 N	19.351	24.328	24.326	62.855
2/5 N	12.9005	16.142	16.147	62.581
1/5 N	6.4503	8.042	8.038	62.306

---

[23] v. Lippmann, Die Chemie der Zuckerarten, I, p. 265; 1904.

As is apparent from column 5 of Table 9 the specific rotation undergoes a considerable dimunition as the concentration of dextrose decreases. A graphic plot showed that the relation was as closely linear as could be judged from the accuracy of the experiments. Mr. Phelps performed a least square adjustment of the straight line representing these values, weighting all points in proportion to the magnitude of the rotation. The result of this computation is the interpolation formula:

$$\left[\alpha\right]^{20.0}_{5461\text{A}} = 62.032 + 0.04257\,c$$

where c is grams of dextrose weighed in vacuo and contained in 100 cc of solution. This formula is valid for values of c between 6 g and 32 g.

From the interpolation formula the values of the rotation at each concentration were calculated and are recorded in column 4 of Table 9. The observed values are in column 3.

It is frequently convenient to express concentration in per cent by weight in vacuo. Consequently, the specific rotation has been found by computation to be the following function of the per cent dextrose:

$$\left[\alpha\right]^{20.0}_{5461\text{A}} = 62.032 + 0.0422\,p + 0.0001897\,p^2$$

In concluding it is a pleasure to acknowledge the assistance rendered by Carl F. Snyder, who made duplicate observations of the rotations measured.

SUMMARY

1. Dextrose obtained from starch conversion products and from invert sugar has been purified by repeated crystallization from aqueous solution. A portion which was subjected to a fractional crystallization showed essential identity in all its fractions. Precipitation by ethyl alcohol produced a similar product.

2. The material after losing its water of crystallization at 60° C was freed from residual moisture by heating in a vacuum at 60° to 80° C for several hours.

3. To prepare the solutions for polarization the dextrose was dried and the final weighing made after it was transferred to the volumetric flask. The substance was dissolved, made to volume at 20°.0 C, and the solution weighed.

4. The data were sufficient for the calculation of the density of dextrose solutions. The following formula, valid between 5 and

30 per cent dextrose, gives densities reliable to 3 or 4 units in the fifth decimal place:

$$D\frac{20^\circ}{4^\circ} = 0.99840 + 0.003788\,p + 0.00001412\,p^2$$

where p is per cent dextrose by weight in vacuo.

5. The normal weight on the saccharimeter scale as determined by Bates and Jackson is 32.231 g weighed in air with brass weights. This weight corresponds exactly with 26.000 g of sucrose and with conversion factors 34.620 for $\lambda = 5892.5$ A and 40.690 for $\lambda = 5461$ A. If the Herzfeld-Schönrock scale (conversion factor 34.657) is used, 32.264 g must be taken to rotate 100.00 S.

6. The rotations at concentrations less than normal are found to deviate considerably from proportionality. A table is given which indicates at 5° S intervals the corrections to be applied to the saccharimeter scale reading.

7. The rotation of the normal solution for $\lambda = 5461$ A is found to be $40\overset{\circ}{.}897$. Since the normal quartz plate rotates $40\overset{\circ}{.}690$, it is shown that the compensation in the quartz-wedge saccharimeter is imperfect and a slightly heterochromatic field results. This results in a lower degree of reproducibility than in the case of sucrose. This is overcome by an increased number of observations and some preliminary experience on the part of the observer.

8. The specific rotation for $\lambda = 5461$ A is found to vary considerably with the concentration of dextrose. It may be represented by the formula,

$$\left[\alpha\right]^{20.0}_{5461\text{A}} = 62.032 + 0.04257\,c$$

when c is grams of anhydrous dextrose weighed in vacuo and contained in 100 cc of solution, or

$$\left[\alpha\right]^{20.0}_{5461\text{A}} = 62.032 + 0.04220\,p + 0.0001897\,p^2$$

where p is per cent anhydrous dextrose by weight in vacuo.

WASHINGTON, July 7, 1916.

FREEZING POINT OF MERCURY

By R. M. Wilhelm, Assistant Physicist.

The temperature at which mercury freezes is of importance in thermometry. It marks the lower limit in the use of mercurial thermometers, and its location at about −39° makes it an important fixed point of the temperature scale below 0° C.

Among the investigators who made precise determinations of this constant may be mentioned Regnault,[1] who in 1862 obtained −38°.50, B. Stewart,[2] 1863, whose value −38°.85 was the result of a very excellent experiment in which a constant volume gas thermometer was used, Vicentini and Omodei[3] in 1888, Chappuis[4] in 1896, and C. Chree[5] in 1898, who obtained the values −38°.80 ±0°.02, −38°.85, and −38°.86, respectively, using mercurial thermometers which had been previously compared with a gas thermometer. The latest determination of this point was made by Henning[6] in 1914. He obtained the value −38°.89, using platinum resistance thermometers which had been compared with a gas thermometer. The above values are fairly consistent and would indicate the freezing point of mercury to be in the neighborhood of −38°.8. However, two determinations of this point, −39°.44 and −39°.38, attributed to Hutchins[7] and Cavendish,[8] who investigated the subject in the period 1776 to 1783, have been published along with the later values and apparently have, in many cases, been given equal weight with them, although these early determinations are obviously entitled to little weight.

---

[1] Mem. d. l'Acad., 26, p. 525; 1862.

[2] Phil. Trans., 153, p. 425; 1863.

[3] Atti della R. Acc. di Torino, 23; 1887.

[4] Compt. rend. de la Conférence Générale, p. 291; 1896.

[5] Phil. Mag., 45, p. 224; 1898.

[6] Annalen der Physik (4), 43, p. 291; 1914.

[7] Phil. Trans.; 1776.

[8] Phil. Trans.; 1783.

All the evidence at present available indicates that the scale defined by the platinum resistance thermometer, when calibrated at 0°, 100°, and 444°6 (the boiling point of sulphur[9]), defines temperatures in agreement with those given by the hydrogen thermometer down to −40° C. A redetermination of the freezing point of mercury on the scale defined by the resistance thermometer seemed, therefore, of value.

SAMPLES OF MERCURY

The freezing points of three different samples of mercury were observed. These three samples were furnished by Mr. McKelvy, of this Bureau, and were designated as "U. S. P.," "Anode," and "Hulett Still." The modes of purification were as follows: U. S. P.: Purified to meet the test requirements of the U. S. Pharmacopœia. Anode: Electrolyzed in a mercurous nitrate solution with the mercury as anode. About 5 per cent was deposited on the cathode to eliminate metals more electropositive than mercury. The product remaining on the anode was then once distilled in vacuum. Hulett Still: An anode sample was distilled in a Hulett still under reduced pressure with a stream of air bubbling through the mercury. The last named of the three samples would thus be considered to be the purest. However, the three samples showed no difference in electromotive properties when used in a normal cadmium cell, nor do the results of the freezing-point determinations indicate the existence of any difference between the three samples.

THERMOMETERS AND MEASURING INSTRUMENTS

The three-resistance thermometers used were selected from a number made by H. K. Griffin, of this Bureau, about a year ago. These thermometers were made with potential terminals and the coils were wound to give a flexible mounting for the wire in the manner described by Waidner and Burgess.[10]

The highest purity Heraeus wire was used for the coils, and short (2 cm) lengths of the same wire were used for the connections between the ends of the coil and the gold lead wires. The glass tubes in which the thermometer coils were inclosed were closed at the top with plugs, sealed in with Khotinski cement, through which the lead wires passed. In this way access of moisture to the coils was prevented. The dimensions and constants of these thermometers are given in the Table 1.

---

[9] Henning used 444°51, but this introduces a difference of only 0.°004 between the two scales at the freezing point of mercury.

[10] Waidner and Burgess, this Bulletin, 6, p. 155; 1910.

TABLE 1

[R_0—mean observed resistance at 0°; F. I.—resistance at 100° minus resistance at 0°; δ—constant in Callendar formula]

Thermometer	R_0	F. I.	$\frac{\text{F. I.}}{R_0}$	δ	Diameter of wire	Length of coil	Internal diameter of tube
					mm	cm	cm
C 28	2.5373	0.99360	0.39160	1.496	0.15	4	0.5
C 24	10.0143	3.9143	.39088	1.496	.1	5	.8
C 22	25.5474	9.9875	.39094	1.495	.1	8	.8

The thermometers were calibrated in the ordinary way at 0°, 100°, and the sulphur boiling point (444°6 at normal pressure). For the calibration use was made of a new sulphur boiling point apparatus to be described by Mueller and Burgess in a paper to appear later in this Bulletin.

The heating effect on the thermometers of the measuring current used was investigated. This effect is proportional to the square of the current and was found to be the same at 0°, 100, and −39°; thus no significant error could have been introduced from this source.

Table 2 shows the magnitude of this effect for the thermometers used.

TABLE 2

Thermometer	Usual measuring current in milliamperes	Heating effect—	
		Per milliampere^2	For usual current
		°C	°C
C 22	2	0.0004	0.0016
C 24	3	0.0003	0.0027
C 28	4	0.0002	0.0032

Three different Wheatstone bridges and also a potentiometer and standard resistance were used in making the resistance measurements. These bridges were designed at this Bureau. The bridges used are described[11] in Scientific Papers 241 and 288. By using a commutator as described by Mueller[12] the resistance between the potential terminals of the thermometers could be measured.

---

[11] This Bulletin, 11, p. 571; 1914. Ibid, 13, p. 547; 1916.

[12] Ibid, 13, p. 556; 1916.

The bridges were calibrated in terms of international ohms, so that they could be used interchangeably. The potentiometer was of the Diesselhorst type made by Otto Wolff. The potentiometer was used to secure a check method but it did not give as high precision, at least with the low resistance thermometer, as the Wheatstone bridge method.

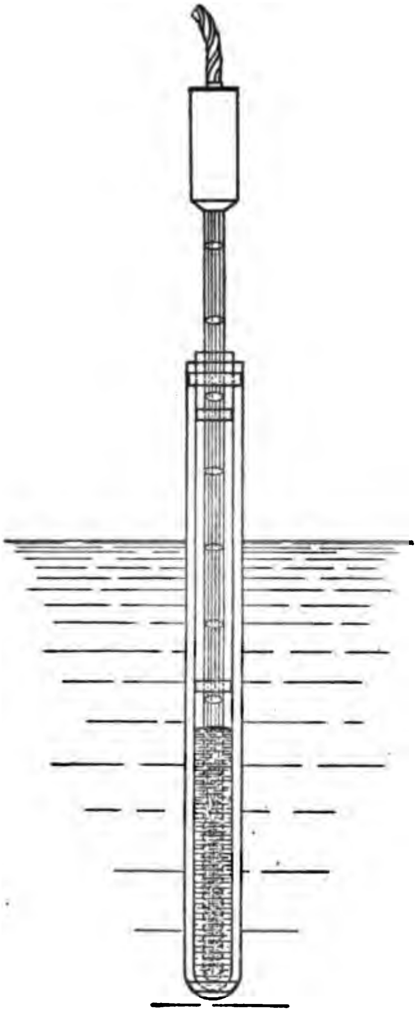


FIG. 1.—*Freezing point tubes with thermometer in position*

METHOD

The mercury was frozen in a glass tube 2 cm inside diameter and about 34 cm long. This tube was inserted in another glass tube 3 cm inside diameter. The thermometer and tubes were held in position by corks. Fig. 1 is a sketch of this apparatus showing one of the thermometers in position. About 38 cc of mercury was used which filled the inner tube to a depth of about 12 cm, which was increased to from 13 to 16 cm when the thermometer was introduced.

In freezing the mercury the tubes containing it were immersed to a depth of about 20 cm in a stirred bath which could be cooled to −50° by expanding carbon dioxide through a coil immersed in a liquid consisting of a mixture of gasoline and carbon tetrachloride. Under these conditions the temperature of the freezing mercury remained constant sometimes for as long as 30 minutes. In some cases where a complete freezing and melting point curve was desired the bath was held at a temperature lower than the freezing temperature until the entire mass of the mercury had frozen and its temperature had begun to fall. If the bath were then allowed to heat up to a temperature higher than the freezing temperature, the melting point could be observed.

PRECAUTIONS

Care was taken to insure that the thermometer coil was sufficiently immersed in the mercury. Conduction down the leads might cause a higher or lower reading, depending on whether the surrounding bath, and thus the air above the mercury, was at a higher or lower temperature than the mercury. Errors from this source would be more likely to occur in the use of thermometer C 22, the coil of which was longer than those of the other two. The effect of raising and lowering the thermometer while the mercury was freezing was observed for C 22. It was found that an immersion of 13 cm (measured from end of tubing) was sufficient to eliminate this source of error. The absence of any disturbing effects due to conduction is also attested by the fact that the results obtained were independent of the outer bath temperature, which varied from below $-50°$ up to $-30°$.

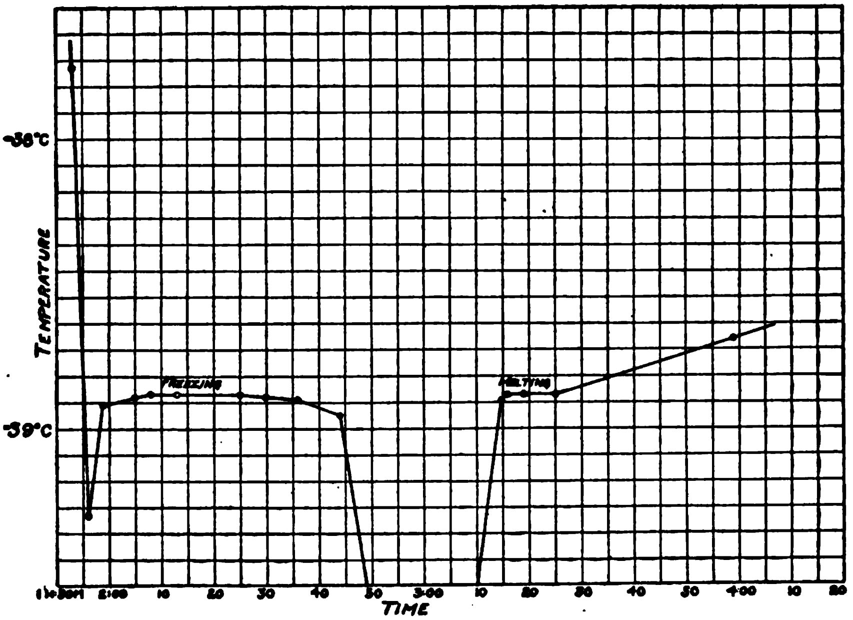


FIG. 2.—*Freezing and melting point curve*

FREEZING AND MELTING POINT CURVES

Fig. 2 shows a typical freezing and melting point curve. A supercooling of several tenths of a degree precedes the constant temperature assumed later when freezing is taking place. No significant difference was noted between the temperatures of the freezing and melting points.

RESULTS

The results are given in Table 3. The mean of the freezing points obtained by the bridge method of resistance measurement with all of the thermometers was −38°.871 for the U. S. P. mercury, −38°.872 for the anode mercury, and −38°.872 for the Hulett still mercury. The mean of all results obtained using the bridge method of resistance measurement is −38°.872, while the mean result by the less precise potentiometer measurements is −38°.875. The mean of all the freezing point determinations is −38°.873 and the mean of the melting point determinations is the same.

TABLE 3

Date	Thermometer	R₀	Rt	t	Sample of mercury	Measuring instruments	Freezing or melting point
1916							
Feb. 7	C 22	25.5473	21.5843	—38.872	Anode	Bridge 11672	Freezing.
Feb. 8	do	25.5472	21.5843	—38.872	do	do	Do.
Do	do	25.5472	21.5845	—38.874	do	do	Melting.
Mar. 11	do	25.5475	21.5844	—38.874	Hulett still	Bridge 1648	Freezing.
Apr. 3	do	25.5475	21.5842	—38.875	do	do	Do.
Mean				—38.873			
Mar. 13	C 22	25.5479	21.5848	—38.874	do	Potentiometer 11576	Do.
1915							
Aug. 14	C 24	10.01438	8.46127	—38.871	do	Bridge 1648	Do.
1916							
Jan. 22	do	10.01438	8.46127	—38.871	U. S. P	Bridge 7481	Do.
Mar. 11	do	10.01402	8.46104	—38.868	Hulett still	Bridge 1648	Do.
Mean				—38.870			
Mar. 13	C 24	10.01416	8.46109	—38.870	do	Potentiometer 11576	Do.
Mar. 20	do	10.01432	8.46087	—38.877	do	do	Do.
Mean				—38.874			
Jan. 19	C 28	2.53740	2.14310	—38.875	U. S. P	Bridge 7481	Melting.
Jan. 27	do	2.53734	2.14311	—38.868	do	do	Do.
Jan. 28	do	2.53731	2.14305	—38.871	do	Bridge 1648	Freezing.
Do	do	2.53731	2.14303	—38.873	do	do	Melting.
Do	do	2.53731	2.14304	—38.872	Anode	Bridge 7481	Freezing.
Mar. 11	do	2.53726	2.14301	—38.870	Hulett still	Bridge 1648	Do.
Mean				—38.872			
Mar. 11	C 28	2.53703	2.14273	—38.875	do	Potentiometer 11576	Do.
Mar. 21	do	2.53729	2.14296	—38.877	do	do	Do.
Mean				—38.876			

These results show that the precision attainable in the determination of the freezing point of mercury is better than 0°.01. It seems probable that the experimental conditions were varied sufficiently in the present work to preclude the possibility of a systematic error of as much as 0°.01 in the result, expressed on the scale defined by the platinum resistance thermometer. The difference between this result (−38°.87) and that found by Henning (−38°.89), also in terms of the scale defined by the platinum resistance thermometer, is greater than would be expected from the accidental errors of either determination. It seems improbable that the discrepancy is due to impurities in the mercury, although it is known that the method of purification used by Henning (distillation in vacuum) [13] is not effective in removing traces of certain metals.

SUMMARY

The freezing point of mercury was determined, using platinum resistance thermometers.

A short historical sketch gives the names of previous investigators, their methods of temperature measurement, and values obtained.

Nineteen determinations were made on three samples of mercury purified by different methods. Three resistance thermometers having resistances in melting ice of approximately 2.5, 10, and 25 ohms, respectively, were used. Resistance measurements were made both by the Wheatstone bridge method and the potentiometer method.

The result of all the measurements gives −38°.873 for the freezing temperature. The maximum deviation of any determination from the mean is 0°.005.

WASHINGTON, August 1, 1916.

---

[13] Geo. A. Hulett and Howard D. Minchin, Phys. Review, **21**, p. 388; 1905.

INDEX TO VOLUME 13.

A.

Acetylene, Determination of, 27.
Acetylene flame, Distribution of energy in visible spectrum of, 355.
Agnew, P. G., W. H. Stannard, and J. L. Fearing, A system of remote control for an electric testing laboratory, 581.
Alloys, Iron-carbon, 1.
Aluminum as oxide, Determination of, 515.
Antenna, Radiotelegraphic, 129.
Apparatus for resistance thermometry, 547.
Aqueous solutions of copper sulphate and sulphuric acid, Density of, 273.

B.

Bates, Frederick, and Richard F. Jackson, Constants of the quartz-wedge saccharimeter and the specific rotation of sucrose. I. The constants for the 26-gram normal weight, 67.
Bingham, Eugene C., Investigation of the laws of plastic flow, 309.
Black body, Luminosity of, 137.
Black body, Spectral radiation of, 459.
Blum, William, Determination of aluminum as oxide, 515.
Bovard, William M., G. W. Vinal and, Inclusions in the silver voltameter deposits, 147.
Bridges, Wheatstone, 547.
Brooks, H. B., and F. C. Weaver, A variable self and mutual inductor, 569.
Burgess, G. K., and R. G. Waltenberg, Further experiments on the volatilization of platinum, 365.
Burns, Keivin, W. F. Meggers, and Paul W. Merrill, Interference measurements of wave lengths in the iron spectrum, 245.
Burrows, Charles W., Correlation of the magnetic and mechanical properties of steel, 173.

C.

Cain, J. R., E. Schramm, and H. E. Cleaves, Preparation of pure iron and iron-carbon alloys, 1.
Calculation of Planck's constant C_2, 535.
Cleaves, H. E., and E. Schramm, J. R. Cain, Preparation of pure iron and iron-carbon alloys, 1.
Coblentz, W. W., Constants of spectral radiation of a uniformly heated inclosure or so-called black body, 459.
——, Sensitivity and magnetic shielding tests of a Thomson galvanometer for use in radiometry. 423.
——, *and W. B. Emerson,* Distribution of energy in the visible spectrum of an acetylene flame, 355.
Color differences in glass screens and tungsten lamps, 287.
Colorimetric determination of acetylene and its application to the determination of water, 27.
Composition and density of aqueous solutions of copper sulphate and sulphuric acid, 273.
Constants of quartz-wedge saccharimeter and the specific rotation of sucrose. I. The constants for the 26-gram normal weight, 67.
Constants of spectral radiation of a uniformly heated inclosure or so-called black body, II, 459.
Control for electric testing laboratory, 581.
Correlation of the magnetic and mechanical properties of steel, 173.
Critically damped galvanometers, Design of, 211.

D.

Damping of waves and other disturbances in mercury, 563
Dellinger, J. H., Calculation of Planck's constant C_2, 535.
——, International system of electric and magnetic units, 599.
Density of aqueous solutions of copper sulphate and sulphuric acid, Relation between composition and, 273.
Determination of acetylene, 27.
Determination of aluminum as oxide, 515.
Dextrose, Rotation of, 633.
Dielectrics, Effect of imperfect, 129.
Distribution of energy in the visible spectrum of an acetylene flame, 355.
Disturbances in mercury, 563.

E.

Effect of imperfect dielectrics in the field of a radiotelegraphic antenna, 129.
Electric and magnetic units, 599.
Electric testing laboratory, System of remote control for, 581.
Emerson, W. B., W. W. Coblentz and, Distribution of energy in the visible spectrum of an acetylene flame, 355.
Energy in the visible spectrum of an acetylene flame, 355.
Experiments on silver voltameter, 479.
Experiments on the volatilization of platinum, 365.

F.

Fairchild, C. O., Paul D. Foote and, Luminosity of a black body and temperature, 137.
Fearing, J. L., and W. H. Stannard, P. G. Agnew, A system of remote control for an electric testing laboratory, 581.
Foote, Paul D., and C. O. Fairchild, Luminosity of a black body and temperature, 137.
Four-terminal resistance standards, Inductance of, 375.

Freezing point of mercury, 655.

Further experiments on the volatilization of platinum, 365.

G.

Galvanometers, Critically damped, 211.

Galvanometer for use in radiometry, Sensitivity and magnetic shielding tests of, 423.

General design of critically damped galvanometers, 211.

Glass screens and tungsten lamps, Photometric comparison of, 287.

Gray, Arthur W., Protected thermoelements, 283.

H.

Heated inclosure, uniformly, Spectral radiation of, 459.

Holler, H. D., and *E. L. Peffer*, Relation between composition and density of aqueous solutions of copper sulphate and sulphuric acid, 273.

I.

Inclusions in the silver voltameter deposits, 147.

Inductance of four-terminal resistance standards, 375.

Inductor, Self and mutual, 569.

Interlaboratory photometric comparison of glass screens and of tungsten lamps, involving color differences, 287.

Interference measurements of wave lengths in the iron spectrum, 245.

International system of electric and magnetic units, 599.

Investigation of the laws of plastic flow, 309.

Iron, Preparation of pure, 1.

Iron spectrum, Interference measurements of wave lengths in, 245.

J.

Jackson, Richard F., Saccharimetric normal weight and the specific rotation of dextrose, 633.

——, *Frederick Bates and*, Constants of the quartz-wedge saccharimeter and the specific rotation of sucrose. I. The constants for the 26-gram normal weight, 67.

L.

Lamps, tungsten, Photometric comparison of glass screens and of, 287.

Laws of plastic flow, 309.

Luminosity of a black body and temperature, 137.

M.

Magnetic and mechanical properties of steel, Correlation of, 173.

Magnetic shielding tests of a Thomson galvanometer, 423.

Magnetic units, Electric and, 599.

Measurements of wave lengths in the iron spectrum, 245.

Mechanical properties of steel, 173.

Meggers, W. F., Keivin Burns, and Paul W. Merrill, Interference measurements of wave lengths in the iron spectrum, 245.

Mercury, Disturbances in, 563.

Mercury, Freezing point of, 655.

Merrill, Paul W., and W. F. Meggers, Keivin Burns, Interference measurements of wave lengths in the iron spectrum, 245.

Middlekauff, G. W., and J. F. Skogland, Interlaboratory photometric comparison of glass screens and of tungsten lamps, involving color differences, 287.

Miller, J. M., Effect of imperfect dielectrics in the field of a radiotelegraphic antenna, 129.

Mueller, E. F., Wheatsone bridges and some accessory apparatus for resistance thermometry, 547.

Mutual inductor, Self and, 569.

N.

Normal weight of dextrose, 633.

Normal weight of sucrose, 67.

O.

Oxide, Aluminum as, 515.

P.

Peffer, E. L., H. D. Holler and, Relation between composition and density of aqueous solutions of copper sulphate and sulphuric acid, 273.

Photometric comparison of glass screens and of tungsten lamps, 287.

Planck's constant C_2, 535.

Plastic flow, 309.

Platinum, Volatilization of, 365.

Preparation of pure iron and iron-carbon alloys, 1.

Protected thermoelements, 283.

Q.

Quartz-wedge saccharimeter, Constants of, 67.

R.

Radiation of a uniformly heated inclosure, 459.

Radiometry, Galvanometer for use in, 423.

Radiotelegraphic antenna, Effect on field of, 129.

Relation between composition and density of aqueous solutions of copper sulphate and sulphuric acid, 273.

Remote control for electric testing laboratory, 581.

Resistance standards, Inductance of four-terminal, 375.

Resistance thermometry, 547.

Rosa, E. B., and G. W. Vinal, Summary of experiments on the silver voltameter at the Bureau of Standards, and proposed specifications, 479.

——, —— Volume effect in the silver voltameter, 447.

Rotation of dextrose, 633.

Rotation of sucrose, 67.

S.

Saccharimeter, Quartz-wedge, 67.

Saccharimetric normal weight and the specific rotation of dextrose, 633.

Schramm, E., J. R. Cain, and H. E. Cleaves, Preparation of pure iron and iron-carbon alloys, 1.

Screens, glass, Photometric comparison of, 287.

Self and mutual inductor, 569.

Sensitivity and magnetic shielding tests of a Thomson galvanometer for use in radiometry, 423.

Silsbee, Francis B., A study of the inductance of four-terminal resistance standards, 375.
Silver voltameter deposits, Inclusions in, 147.
Silver voltameter, Experiments on, 479.
Silver voltameter, Volume effect in, 447.
Skogland, J. F., G. W. Middlekauff and, Interlaboratory photometric comparison of glass screens and of tungsten lamps, involving color differences, 287.
Specifications for silver voltameter, 479.
Specific rotation of dextrose, 633.
Spectral radiation of a uniformly heated inclosure, 459.
Spectrum, Visible, of an acetylene flame, 355.
Stannard, W. H., P. G. Agnew, and J. L. Fearing, A system of remote control for an electric testing laboratory, 581.
Steel, Magnetic and mechanical properties of, 173.
Stillman, M. H., Damping of waves and other disturbances in mercury, 563.
Study of the inductance of four-terminal resistance standards, 375.
Sucrose, Rotation of, 67.
Sulphuric acid, copper sulphate and, Density of aqueous solutions of, 273.
Summary of experiments on the silver voltameter at the Bureau of Standards and proposed specifications, 479.
System of electric and magnetic units, 599.
System of remote control for an electric testing laboratory, 581.

T.

Temperature, Luminosity of a black body and, 137.
Thermoelements, Protected, 283.
Thermometry, Resistance, 547.
Thomson galvanometer for use in radiometry, 423.
Tungsten lamps, Photometric comparison of glass screens and of, 287.

U.

Units, magnetic, Electric and, 599.

V.

Variable self and mutual inductor, 569.
Vinal, G. W., and William M. Bovard, Inclusions in the silver voltameter deposits, 147.
——, *E. B. Rosa and*, Summary of experiments on the silver voltameter at the Bureau of Standards and proposed specifications, 479.
——, ——, Volume effect in the silver voltameter, 447.
Visible spectrum of an acetylene flame, 355.
Volatilization of platinum, 365
Voltameter, Deposits in, 147.
Voltameter, silver, Volume effect in, 447.
Voltameter, silver, Summary of experiments on, 479.
Volume effect in the silver voltameter, 447.

W.

Wallenberg, R. G., G. K. Burgess and, Further experiments on the volatilization of platinum, 365.
Water, Determination of, 27.
Waves, Damping of, 563.
Weaver, E. R., Colorimetric determination of acetylene and its application to the determination of water, 27.
Weaver, F. C., H. B. Brooks and, A variable self and mutual inductor, 569.
Weight, Saccharimetric normal, 633.
Wenner, Frank, General design of critically damped galvanometers, 211.
Wheatstone bridges and some accessory apparatus for resistance thermometry, 547.
Wilhelm, R. M., Freezing point of mercury, 655.

⁂

14 DAY USE
RETURN TO DESK FROM WHICH BORROWED
LOAN DEPT.
This book is due on the last date stamped below, or
on the date to which renewed.
Renewed books are subject to immediate recall.

REC'D
JUL 9 '67 -3 PM
LOAN DEPT.
NOV 8 1967 3 2
REC'D
NOV 1 '67 -3 PM
LOAN DEPT.
OCT 17 1968 3 7
RECEIVED
~~OCT 14 '68 -3 PM~~
~~JAN 29 1970 3 8~~
REC'D LD JAN 19 '70 -9 AM

NOV 14 1974
JUN 15 2004
REC'D CIRC DEPT OCT 23 '74

LD 21A-60m-7,'66
(G4427s10)476B
MAR 12 1980
General Library
University of California
Berkeley
REC '80

U.C. BERKELEY LIBRARIES

C006693035

351540

U.S.A.

UNIVERSITY OF CALIFORNIA LIBRARY